

A Fixed Point Theorem in Banach Space

by

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The present note contains a fixed point theorem for a completely continuous operator in a Banach space. This theorem is based on the notion of the degree of mapping in the sense of Leray-Schauder [2]. As a particular case of this theorem we obtain a theorem of M. A. Krasnoselskii [1], who has also given an application of his theorem to the theory of non-linear integral equations of Hammerstein's type.

1. Let X be an arbitrary Banach space. Denote by Q the sphere in X with centre in θ and radius r , where θ is the zero-element in X , i. e. the set of all elements of X satisfying the inequality $\|x\| \leq r$. The boundary of Q , i. e. the set of all elements of X satisfying the equation $\|x\| = r$, is denoted by S .

Let F be a completely continuous operator (in general non-linear) defined on S with range in X . Consider the continuous operator

$$\Phi = I - F$$

defined on S , where I is the identical transformation of X . Suppose that

$$(1) \quad \Phi(x) \neq 0 \quad \text{for every } x \text{ of } S.$$

Then, following Leray and Schauder [2], we can define the degree $d[\Phi, Q, 0]$ of the mapping Φ .

The following theorem is true.

THEOREM 1. *Let us assume that on the boundary S of the sphere Q a continuous mapping $\Phi(x) = x - F(x)$ is defined, where F is a completely continuous operator, satisfying condition (1) and the following condition*

$$(2) \quad \|x - F(x)\|^2 \geq \|F(x)\|^2 - \|x\|^2 \quad \text{for every } x \text{ of } S.$$

Then the degree of Φ is one.

Theorem 1 implies the following fixed point theorem.

THEOREM 2. *Let F be a completely continuous operator defined on the sphere Q and satisfying condition (2). Under these assumptions F possesses a fixed point in Q , i. e. there exists an element x_0 in Q such that*

$$F(x_0) = x_0.$$

The condition

$$(3) \quad \|x - F(x)\| \geq \|F(x)\| \quad \text{for every } x \text{ of } S$$

is evidently stronger than condition (2). Hence it appears that the following theorem is a particular case of Theorem 2.

THEOREM 3. *Let F be a completely continuous operator defined on the sphere Q and satisfying condition (3). Then F possesses a fixed point in Q .*

It is also obvious that the condition

$$(4) \quad \|F(x)\| \leq \|x\| \quad \text{for every } x \text{ of } S,$$

implies condition (2). Thus we obtain the following theorem of E. Rothe [3] as a particular case of Theorem 2.

THEOREM 4. *Let F be a completely continuous operator defined on the sphere Q and satisfying condition (4). Then F possesses a fixed point in Q .*

2. Now let us assume that H is a real Hilbert space. We use here the same designations as in section 1.

It is easy to verify that in a real Hilbert space condition (2) and the condition

$$(5) \quad (F(x), x) \leq (x, x) \quad \text{for every } x \text{ of } S$$

are equivalent. Hence, in a real Hilbert space Theorem 1 can be formulated as follows:

THEOREM 5. *Let F be a completely continuous operator defined on the boundary S of the sphere Q of a real Hilbert space. If the operator F satisfies conditions (1) and (5) then the degree of Φ is one.*

Now if we state Theorem 2 for a real Hilbert space then we obtain the following theorem of Krasnoselskiĭ [1].

THEOREM 6. *Let F be a completely continuous operator defined on the sphere Q of a real Hilbert space. If the operator F satisfies condition (5) then F possesses a fixed point in Q .*

Remark 1. In all the above theorems, instead of the sphere Q we can take an arbitrary open bounded set containing the zero-element of the space. Then S will be the boundary of the corresponding open set. In this case all these theorems remain true.

Let F be a completely continuous operator defined on the sphere Q of a real Hilbert space. Now suppose that $F(x)$ is differentiable in the

sense of Fréchet at the point θ . Denote by $A=F'(\theta)$ the Fréchet differential at the point θ . Suppose also that the Fréchet differential satisfies the following condition:

$$(6) \quad (Ax, x) \leq 0 \quad \text{for every } x \text{ of } H.$$

Now the following theorem can be proved.

THEOREM 7. *Let F be a completely continuous operator defined on the sphere Q of a real Hilbert space. Let us assume that the following conditions are satisfied:*

1° $F(\theta) = \theta$; 2° at the point θ $F(x)$ has a Fréchet differential $F'(\theta) = A$, satisfying condition (6).

Under these assumptions if ε is a positive number not greater than r and if Q_ε is the sphere with centre in θ and radius ε then the image of Q_ε under the transformation $\Phi(x) = x - F(x)$ contains a sphere K_ε with centre in θ , i. e. $\Phi(Q_\varepsilon) \supset K_\varepsilon$.

The proof of Theorem 7 is based on Theorem 6.

3. This section contains some remarks concerning the application of Galerkin's method to equation

$$(7) \quad F(x) = x.$$

It appears that Galerkin's approaches to the solution of equation (7) always exist when condition (5) is fulfilled. We shall give a more precise formulation of this fact.

Let $\{e_n\}$ ($n=1, 2, \dots$) be an orthonormal complete system in a separable Hilbert space H . Denote by H_n the n -dimensional space spanned by the elements e_i ($i=1, 2, \dots, n$). If x_n is of the form

$$(8) \quad x_n = \sum_{i=1}^n c_i^{(n)} e_i,$$

where the numbers $c_i^{(n)}$ are defined by the system of equations

$$(9) \quad (Fx_n, e_i) = c_i^{(n)} \quad (i=1, 2, \dots, n)$$

then x_n is a Galerkin approach to the solution of equation (7).

THEOREM 8. *Let F be a completely continuous operator defined on the sphere Q of a real separable Hilbert space H with range in H . If F satisfies condition (5) then for every n ($n=1, 2, \dots$) there exists a Galerkin approach $x_n \in H_n \cdot Q$. If $\{x_n\}$, where $x_n \in H_n \cdot Q$, is a sequence of Galerkin's approaches, then there exists a sub-sequence $\{x_{n_p}\}$ which converges to a solution of equation (7). Every convergent sub-sequence $\{x_{n_p}\}$, $x_{n_p} \in H_{n_p} \cdot Q$ of Galerkin's approaches converges to a solution of equation (7). If equation (7)*

possesses at most one solution in Q then the sequence $\{x_n\}$, $x_n \in H_n \cdot Q$ of Galerkin's approaches converges to the solution of equation (7).

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On the Solution of Linear Algebraic Equations

by

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1. Paper [1] gives an application of the biorthogonalisation method to the theory of bilinear forms. In the present paper we give an application of this method to the solution of linear algebraic equations. It appears that the most important methods used for solving linear algebraic equations can be deduced from the biorthogonalisation method given below. This applies for instance to Gauss method of elimination, Cholesky's method, Banachiewicz's method of krakovians, Morris' escalator method, and the method of orthogonal vectors given by Fox, Huskey, and Wilkinson for symmetrical equations and generalised by Grossman. It will also be shown that all these methods coincide in essence but are different with respect to the organisation of the reckoning process. Thus we have also found the geometrical sense of various algebraic methods. The orthogonalisation method given below may also be regarded as a particular case of the biorthogonalisation method.

2. Let X be an n -dimensional linear space and let A be a linear transformation of X into itself. Let us suppose that A is one-to-one, although this is not essential to the method. Consider the linear equation

$$(1) \quad Ax = b, \quad x, b \in X.$$

Let x_i and y_i ($i=1, 2, \dots, n$) be two bases in X , which may be identical. Put $e_i = Ax_i$ ($i=1, 2, \dots, n$). We shall apply the biorthogonalisation process of [1] to system $(e_i; y_i)$, where y_i ($i=1, 2, \dots, n$) are considered as linearly independent linear functionals on X .

Set

$$(2) \quad \begin{aligned} \bar{e}_1 &= e_1 \quad \text{and} \quad \bar{y}_1 = y_1 \quad e_i = Ax_i, \\ \bar{e}_{k+1} &= e_{k+1} - \sum_{i=1}^k \frac{l}{(\bar{e}_i, \bar{y}_i)} (e_{k+1}, \bar{y}_i) \bar{e}_i, \\ \bar{y}_{k+1} &= y_{k+1} - \sum_{i=1}^k \frac{l}{(\bar{e}_i, \bar{y}_i)} (\bar{e}_i, y_{k+1}) y_i, \end{aligned}$$

provided that one of the bases is so ordered that $(\bar{e}_i, \bar{y}_i) \neq 0$ for $i=1, 2, \dots, n$.

We have

$$(2') \quad (\bar{e}_k, \bar{y}_i) = 0 \quad \text{for} \quad i \neq k.$$

Put $(\bar{e}_i, \bar{y}_i) = d_i$, $(e_k, \bar{y}_i) = v_{ki}$, $(\bar{e}_i, y_k) = u_{ki}$ and $b_{ki} = \frac{l}{d_i} u_{ki}$, $c_{ki} = \frac{l}{d_i} v_{ki}$ for $i < k$ and $b_{ki} = c_{ki} = 0$ for $i > k$ and $b_{kk} = c_{kk} = l$ for $i = 1, 2, \dots, n$.

We have [1]

$$u_{k1} = a_{1k}; \quad v_{k1} = a_{k1},$$

$$(3) \quad u_{kj} = a_{jk} - \sum_{i=1}^{j-1} \frac{l}{d_i} v_{ji} u_{ki}; \quad v_{kj} = a_{kj} - \sum_{i=1}^{j-1} \frac{l}{d_i} u_{ji} v_{ki}, \quad (j = 2, \dots, k-1).$$

$$d_k = a_{kk} - \sum_{i=1}^{k-1} \frac{l}{d_i} v_{ki} u_{ki}, \quad \text{where} \quad a_{kj} = (e_j, y_k).$$

Further we have [1]

$$(4) \quad a_{kj} = \sum_{i=1}^{k-1} c_{ki} d_i b_{ji} \quad (k, j = 1, 2, \dots, n).$$

If $A \begin{pmatrix} 1, 2, \dots, p \\ 1, 2, \dots, p \end{pmatrix}$ denotes the principal minor of $\|a_{ki}\|$ for $p = 1, 2, \dots, n$ then we get [1]

$$(5) \quad A \begin{pmatrix} 1, 2, \dots, p \\ 1, 2, \dots, p \end{pmatrix} = d_1 \cdot d_2 \cdot \dots \cdot d_p \quad \text{for} \quad (p = 1, 2, \dots, n).$$

Consider the transformations [1]

$$(6) \quad e_k = \bar{e}_k + \sum_{i=1}^{k-1} b_{ki} \bar{e}_i$$

or

$$x_k = \bar{x}_k + \sum_{i=1}^{k-1} b_{ki} \bar{x}_i, \quad \text{where} \quad \bar{x}_1 = x_1, \quad A \bar{x}_k = \bar{e}_k \quad (k = 1, 2, \dots, n)$$

and

$$(7) \quad y_k = \bar{y}_k + \sum_{i=1}^{k-1} \bar{c}_{ki} \bar{y}_i \quad (k = 1, 2, \dots, n),$$

If $b = \sum_{i=1}^n a_i \bar{e}_i$ then $a_i = (b, \bar{y}_i) / d_i$ ($i = 1, 2, \dots, n$) by (2').

Hence, $b = \sum_{i=1}^n \frac{1}{d_i} (b, \bar{y}_i) A \bar{x}_i = A \sum_{i=1}^n \frac{1}{d_i} (b, \bar{y}_i) \bar{x}_i$.

Thus $x = \sum_{i=1}^n \frac{1}{d_i} (b, \bar{y}_i) \bar{x}_i$ is the solution of equation (1). We have by (7)

$$(8) \quad (b, \bar{y}_1) = (b, y_1) \quad \text{and} \quad (b, \bar{y}_k) = (b, y_k) - \sum_{i=1}^{k-1} c_{ki} (b, \bar{y}_i) = (b, y_k) - \sum_{i=1}^{k-1} v_{ki} (b, \bar{y}_i) / d_i.$$

Suppose that $b = \sum_{i=1}^n t_i e_i$. Then multiplying (6) by t_i and summing from $i=1$ to $i=n$, we get

$$(9) \quad t_n = (b, \bar{y}_n) / d_n; \quad t_k = (b, \bar{y}_k) / d_k - \sum_{i=k+1}^n b_{ki} t_i \quad (k = n-1, \dots, 1).$$

Hence, $x = \sum_{i=1}^n t_i x_i$ is the solution of equation (1).

Remark. 1. We have used the notion of the scalar product, since it is very convenient, but it is not necessary in applying the above method. For this aim it is sufficient to apply only the notion of the linear functional. In fact, we can apply the biorthogonalisation process to system $(Ax_i; f_i)$, where f_i ($i=1, 2, \dots, n$) are arbitrary linearly independent linear functionals on X .

Now consider the system of linear algebraic equations

$$(10) \quad \sum_{j=1}^n a_{kj} t_j = b_k \quad (k=1, 2, \dots, n).$$

In this case the linear operator A is defined by the matrix $\|a_{kj}\|$. In order to show that the methods mentioned in the introduction can be deduced from the biorthogonalisation method we use the basis

$$(x_k) = (y_k) = (\varphi_k), \quad \text{where} \quad \varphi_1 = (1, 0, \dots), \quad \varphi_2 = (0, 1, 0, \dots), \dots$$

Then we have $(A\varphi_j, \varphi_k) = a_{kj}$ ($k, j=1, 2, \dots, n$); using (3) and putting in (8) $(b, y_i) = (b, \varphi_i) = b_i$ ($i=1, 2, \dots, n$) we obtain the solution defined by (9).

It is evident that we must assume

$$(11) \quad A \begin{pmatrix} 1, 2, \dots, p \\ 1, 2, \dots, p \end{pmatrix} \neq 0 \quad \text{for} \quad p=1, 2, \dots, n.$$

Formula (4) gives a decomposition of a matrix into triangle matrices or into Banachiewicz's canonical krakovians.

Formula (5) shows that the decomposition is the same as that obtained by the Gaussian algorithm ([2], p. 38). Thus we see that the algebraical decomposition of a matrix into triangle matrices is a biorthogonalisation process.

It is obvious that the algebraical part of the method in question is the same as Banachiewicz's, which is in essence a shortening of Gauss' elimination method ([3] p. 249).

If A is a real symmetrical matrix then the matrices $\|c_{ki}\|$ and $\|b_{ki}\|$ coincide [1] and we obtain the method of Cholesky-Banachiewicz ([3], p. 249). Hence it appears that these algebraic operations have a simple geometric sense consisting of the biorthogonalization process and of passing from one basis to another.

It is easy to see that the method of orthogonal vectors given by Fox, Huskey and Wilkinson [4] and also its generalisation by Grossman [5] can be obtained by the biorthogonalisation method. Grossman has shown that Morris' escalator method and the method of orthogonal vectors are equivalent. Thus Morris' method can also be deduced from the biorthogonalisation method, which can also be obtained by direct reckoning. Thus we have shown that the above-mentioned methods are in essence equivalent and can be deduced from the biorthogonalisation method.

3. The orthogonalisation method. Let A be an arbitrary linear transformation of X into itself and let (y_i) , $(i=1, 2, \dots, n)$ be a basis in X . Applying the orthogonalisation process to system $(e_i) = (Ay_i)$, $(i=1, 2, \dots, n)$ we have

$$(12) \quad (A\bar{y}_k, A\bar{y}_i) = 0 \quad \text{for} \quad i \neq k,$$

where

$$(13) \quad \bar{y}_1 = y_1, \quad \bar{y}_{k+1} = y_{k+1} - \sum_{i=1}^k \frac{1}{\|A\bar{y}_i\|^2} (Ay_{k+1}, A\bar{y}_i) \bar{y}_i$$

and

$$A\bar{y}_1 = Ay_1, \quad A\bar{y}_{k+1} = Ay_{k+1} - \sum_{i=1}^k \frac{1}{\|A\bar{y}_i\|^2} (Ay_{k+1}, A\bar{y}_i) A\bar{y}_i.$$

Put

$$\alpha_{ki} = (Ay_k, Ay_i), \quad (k, i = 1, 2, \dots, n) \quad \beta_{ki} = (Ay_k, \bar{y}_i) \quad \text{for} \quad i < k.$$

Then we get [1]

$$\beta_{ki} = \alpha_{ki} \quad \text{for} \quad k = 1, 2, \dots, n; \quad \beta_{kj} = \alpha_{kj} - \sum_{i=1}^{j-1} \frac{1}{\beta_{ji}} \bar{\beta}_{ji} \beta_{ki} \quad \text{for} \quad j = 1, 2, \dots, k,$$

where

$$\beta_{kk} = (A\bar{y}_k, A\bar{y}_k) = \|A\bar{y}_k\|^2 \quad \text{for} \quad k = 1, 2, \dots, n.$$

If $\beta_{kk} \neq 0$ for $k = 1, 2, \dots, n$ then for every b we have

$$(14) \quad b = \sum_{i=1}^n \frac{1}{\|A\bar{y}_i\|^2} (b, A\bar{y}_i) A\bar{y}_i = A \sum_{i=1}^n \frac{1}{\|A\bar{y}_i\|^2} (b, A\bar{y}_i) \bar{y}_i = Ax.$$

Thus $x = \sum_{i=1}^n \frac{1}{\|A\bar{y}_i\|^2} (b, A\bar{y}_i) \bar{y}_i$ is the solution of equation (1) and A is one-to-one since the Ay_i , $(i=1, 2, \dots, n)$ are linearly independent by (12)

and (y_k) is a basis in X by (13), (12). Since, by (13), Ay_k is a linear combination of the $A\bar{y}_i$, $(i=1,2,\dots,k)$ for $k=1,2,\dots,n$, we infer that b is a linear combination of the $A\bar{y}_i$ if, and only if, b is a linear combination of the Ay_i , $(i=1,2,\dots,n)$. Hence we conclude: there exists a solution of equation (1) or (10) if, and only if, b is a linear combination of the Ay_i , $(i=1,2,\dots,n)$. If there are only p numbers $\beta_{kk} \neq 0$ then the system (Ay_i) contains only p linearly independent vectors.

As a result of (13) and (14) the solution $x = \sum_{i=1}^n t_i y_i$ of equation (1) is given by the following formulas:

$$(15) \quad (b, A\bar{y}_1) = (b, Ay_1), \quad (b, A\bar{y}_k) = (b, Ay_k) - \sum_{i=1}^{k-1} \frac{1}{\beta_{ii}} \bar{\beta}_{ki} (b, Ay_i),$$

$$(16) \quad t_n = \frac{1}{\beta_{nn}} (b, A\bar{y}_n); \quad t_i = \frac{1}{\beta_{ii}} (b, Ay_i) - \sum_{j=i+1}^{k-1} \frac{1}{\beta_{jj}} \beta_{ji} t_j \quad \text{for } i=n-1, n-2, \dots, 2, 1.$$

For the solution of equation (10) it is convenient to take

$$(y_i) = (\varphi_i), \quad \text{where} \quad \varphi_1 = (1, 0, 0, \dots), \quad \varphi_2 = (0, 1, 0, \dots) \dots$$

For the sake of simplicity let us assume A to be one-to-one. Then in (2), for the basis (x_i) use the basis (y_i) and for (y_i) use (Ay_i) . Since $(Ay_k, Ay_i) = (A\bar{y}_i, Ay_k)$, we obtain for (3) $\bar{u}_{ki} = v_{ki} = \beta_{ki}$ and $\bar{d}_i = \beta_{ii}$, where $e_k = Ay_k$ and $\bar{e}_k = A\bar{y}_k$ and \bar{y}_k is defined as \bar{x}_k in (6). Formulas (15) and (16) result from (8) and (9). Thus we see that the orthogonalisation method is a particular case of the biorthogonalisation method.

Remark 2. If the matrix $\|a_{kj}\|$ in (10) is real symmetrical and positively defined then the biorthogonalisation of the systems $(A\varphi_i)$, (φ_i) coincides with the orthogonalisation of the system (φ_i) in a new metric defined by the scalar product $[x, y] = (Ax, y)$. Thus Banachiewicz's square root method ([6], p. 85) may be regarded as an orthogonalisation process.

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A Generalisation of Jacobi's Method for Bilinear Forms

by

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This note concerns bilinear forms defined on the product of two linear spaces of finite dimension; a generalisation of the reduction of a Hermitian bilinear form to canonical form is considered. It is shown that canonical reduction is also possible in the general case if the canonical basis is replaced by two canonical bases. The method used here is based on the biorthogonalisation process. It is shown that in the classical case of Hermitian bilinear forms the biorthogonalisation method coincides with Jacobi's method.

1. Let X be an n -dimensional linear space and x_1, x_2, \dots, x_n a basis in this space. Consider n linearly independent linear functionals f_1, f_2, \dots, f_n on X . A system $(x_i; f_i)$, $i=1, 2, \dots, n$ is called biorthogonal if $f_i(x_i) \neq 0$ and $f_i(x_k) = 0$ for $i \neq k$. We shall apply the well known biorthogonalisation process to our system $(x_i; f_i)$, $i=1, 2, \dots, n$.

Put $\bar{x}_1 = x_1$. There exists a linear functional f_k such that $f_k(x_1) \neq 0$. Suppose that f_1 is the first linear functional having this property, i. e. $f_1(x_1) \neq 0$. Then we put

$$\bar{f}_1 = f_1 \quad \text{and} \quad \bar{f}_2 = f_2 - \frac{f_2(\bar{x}_1)}{\bar{f}_1(\bar{x}_1)} \bar{f}_1.$$

The sequence $\left(x_i - \frac{\bar{f}_1(x_i)}{\bar{f}_1(\bar{x}_1)} \bar{x}_1\right)$, $i=1, 2, \dots, n$ contains an element for which \bar{f}_2 does not vanish. Suppose that $x_2 - \frac{\bar{f}_1(x_2)}{\bar{f}_1(\bar{x}_1)} \bar{x}_1$ is the first of these elements. Then we put $\bar{x}_2 = x_2 - \frac{\bar{f}_1(x_2)}{\bar{f}_1(\bar{x}_1)} \bar{x}_1$. We have $\bar{f}_2(\bar{x}_1) = 0$, $\bar{f}_1(\bar{x}_2) = 0$ and

$$\bar{f}_2(\bar{x}_2) = f_2(x_2) - \frac{1}{\bar{f}_1(\bar{x}_1)} \bar{f}_1(x_2) f_2(\bar{x}_1) \neq 0.$$

We repeat the process with the same assumptions concerning the order of the basis (x_i) , $i=1, 2, \dots, n$ and assume that \bar{x}_i , \bar{f}_i , $f_i(\bar{x}_j)$ and

$\bar{f}_j(x_i)$ are defined for $i=1,2,\dots,k$, $j=1,2,\dots,i-1$, and $\bar{f}_k(\bar{x}_j)=0$ for $j \neq k$. Then we set

$$(1) \quad \bar{f}_{k+1} = f_{k+1} - \sum_{i=1}^k \frac{1}{\bar{f}_i(\bar{x}_i)} f_{k+1}(\bar{x}_i) \bar{f}_i.$$

The sequence $\left(x_j - \sum_{i=1}^k \frac{1}{\bar{f}_i(\bar{x}_i)} \bar{f}_i(x_j) \bar{x}_i\right)$ contains an element for which \bar{f}_{k+1} does not vanish. Suppose that its index is exactly $j=k+1$; then we put

$$(2) \quad \bar{x}_{k+1} = x_{k+1} - \sum_{i=1}^k \frac{1}{\bar{f}_i(\bar{x}_i)} \bar{f}_i(x_{k+1}) \bar{x}_i.$$

By (1) and (2) we have

$$(3) \quad f_{k+1}(\bar{x}_j) = f_{k+1}(x_j) - \sum_{i=1}^{j-1} \frac{1}{\bar{f}_i(\bar{x}_i)} \bar{f}_i(x_j) f_{k+1}(\bar{x}_i) \quad \text{for } j=1,2,\dots,k$$

$$(4) \quad \bar{f}_j(x_{k+1}) = f_j(x_{k+1}) - \sum_{i=1}^{j-1} \frac{1}{\bar{f}_i(\bar{x}_i)} f_j(\bar{x}_i) \bar{f}_i(x_{k+1}) \quad \text{for } j=1,2,\dots,k$$

$$(5) \quad \bar{f}_{k+1}(\bar{x}_{k+1}) = f_{k+1}(x_{k+1}) - \sum_{i=1}^k \frac{1}{\bar{f}_i(\bar{x}_i)} f_{k+1}(\bar{x}_i) \bar{f}_i(x_{k+1}).$$

If $j > k$ then $f_k(\bar{x}_j)=0$ by (1). Hence, by (2)

$$(6) \quad f_k(x_j) = \sum_{i=1}^{j-1} \frac{1}{\bar{f}_i(\bar{x}_i)} \bar{f}_i(x_j) f_k(\bar{x}_i) = \sum_{i=1}^n \frac{1}{\bar{f}_i(\bar{x}_i)} \bar{f}_i(x_j) f_k(\bar{x}_i) \quad \text{for } j > k.$$

If $j < k$ then $\bar{f}_k x_j = 0$ by (2). Hence, by (1)

$$(7) \quad f_k(x_j) = \sum_{i=1}^{k-1} \frac{1}{\bar{f}_i(\bar{x}_i)} f_k(\bar{x}_i) \bar{f}_i(x_j) = \sum_{i=1}^n \frac{1}{\bar{f}_i(\bar{x}_i)} f_k(\bar{x}_i) \bar{f}_i(x_j) \quad \text{for } j < k.$$

Consider the biorthogonal transformations defined by (1), (2)

$$(8) \quad x_k = \sum_{i=1}^k b_{ki} \bar{x}_i \quad \text{and} \quad f_k = \sum_{i=1}^k c_{ki} \bar{f}_i, \quad (k=1,2,\dots,n),$$

where

$$(9) \quad \begin{cases} b_{kk} = c_{kk} = 1; & \bar{f}_k(\bar{x}_k) = d_k, & \bar{f}_i(x_k) = u_{ki}, & f_k(\bar{x}_i) = v_{ki} & \text{and} \\ b_{ki} = \frac{1}{d_i} u_{ki}, & c_{ki} = \frac{1}{d_i} v_{ki} & \text{for } i < k & \text{and } b_{ki} = c_{ki} = 0 & \text{for } i > k. \end{cases}$$

By (3), (4) and (5) we have the following recurrent formulas

$$(10) \quad \left\{ \begin{array}{l} u_{kj} = a_{jk} - \sum_{i=1}^{j-1} \frac{1}{d_i} v_{ji} u_{ki}; \quad v_{kj} = a_{kj} - \sum_{i=1}^{j-1} \frac{1}{d_i} u_{ji} v_{ki}, \\ d_k = a_{kk} - \sum_{i=1}^{k-1} \frac{1}{d_i} v_{ki} u_{ki}, \quad \text{where} \quad a_{kj} = f_k(x_j) \quad j = 1, 2, \dots, k-1. \end{array} \right.$$

By (6), (7) and (9) we have

$$a_{kj} = \sum_{i=1}^n \frac{1}{d_i} u_{ji} v_{ki} = \sum_{i=1}^n b_{ji} d_i c_{ki} \quad \text{for} \quad j \neq k.$$

From (5) and (9) it follows that

$$(11) \quad a_{kj} = \sum_{i=1}^n b_{ji} d_i c_{ki} = \sum_{i=1}^n c_{ki} d_i b_{ji} \quad k, j = 1, 2, \dots, n.$$

Substituting $b'_{ij} = b_{ji}$ in (11) we obtain

$$(12) \quad a_{kj} = \sum_{i=1}^n c_{ki} d_i b'_{ij}$$

or

$$(13) \quad \|a_{kj}\| = \|c_{ki}\| \cdot \|d_i\| \|b'_{ij}\|,$$

where $\|d_i\|$ is the diagonal matrix and $\|b'_{ij}\|$ denotes the transposition of $\|b_{ij}\|$.

Denote by $A \begin{pmatrix} 1, 2, \dots, p \\ 1, 2, \dots, p \end{pmatrix}$ the principal minor of the matrix $A = \|a_{kj}\|$. Since the determinants of $\|b'_{ij}\|$ and $\|c_{ki}\|$ equal 1 and by (13) we have

$$(14) \quad A \begin{pmatrix} 1, 2, \dots, p \\ 1, 2, \dots, p \end{pmatrix} = d_1 d_2 \dots d_p \quad \text{for} \quad p = 1, 2, \dots, n,$$

hence $d_p \neq 0$ for $p = 1, 2, \dots, n$ if, and only if,

$$A \begin{pmatrix} 1, 2, \dots, p \\ 1, 2, \dots, p \end{pmatrix} \neq 0 \quad \text{for} \quad p = 1, 2, \dots, n.$$

If $f = \sum_{i=1}^n \eta_i \bar{f}_i$ and $x = \sum_{i=1}^n \xi_i \bar{x}_i$ then we have

$$(15) \quad \eta_i = \frac{1}{d_i} f(\bar{x}_i) \quad \text{and} \quad \xi_i = \frac{1}{d_i} \bar{f}_i(x).$$

Thus we obtain a canonical form for $f(x)$

$$(16) \quad f(x) = \sum_{i=1}^n d_i \xi_i \eta_i = \sum_{i=1}^n \frac{1}{d_i} \bar{f}_i(x) f(\bar{x}_i).$$

Putting $\tilde{f}_i = \frac{1}{d_i} \bar{f}_i$ in (16) we get

$$(17) \quad f(x) = \sum_{i=1}^n \tilde{f}_i(x) f(\bar{x}_i) \quad \text{and} \quad \tilde{f}_k(x_k) = \delta_k, \quad i=1, 2, \dots, n,$$

where δ_{kl} is the Kronecker symbol.

2. Now let X and Y be two n -dimensional linear spaces. We shall say that $A(x, y)$ is a Hermitian bilinear functional on the Cartesian product $X \times Y$ if for a fixed y $A(x, y)$ is a linear functional on X and for a fixed x , $A(x, y)$ is a linear functional on Y of the second kind, i. e. $A(x, \alpha y_1 + \beta y_2) = \bar{\alpha} A(x, y_1) + \bar{\beta} A(x, y_2)$, where $\bar{\alpha}$ and $\bar{\beta}$ are complex numbers conjugate to α, β . Let (x_i) be a basis in X and (y_i) a basis in Y . Then $f_i(x) = A(x, y_i)$, $i=1, 2, \dots, n$ is a linear functional on X . Hence we can apply the biorthogonalisation method of 1 to reduce $A(x, y)$ to canonical form.

Substituting $\bar{f}_i(x) = A(x, \bar{y}_i)$ in 1, we obtain

$$(18) \quad \begin{aligned} \bar{x}_1 &= x_1 \quad \text{and} \quad \bar{y}_1 = y_1, \\ \bar{x}_2 &= x_2 - \frac{1}{A(\bar{x}_1, \bar{y}_1)} A(x_2, \bar{y}_1) \bar{x}_1; \end{aligned}$$

$$\bar{f}_2(x) = f_2(x) - \frac{A(\bar{x}_1, y_2)}{A(\bar{x}_1, \bar{y}_1)} \bar{f}_1(x) = A\left(x, y_2 - \frac{1}{A(\bar{x}_1, \bar{y}_1)} A(\bar{x}_1, y_2) \bar{y}_1\right);$$

hence

$$\bar{y}_2 = y_2 - \frac{1}{\overline{A(\bar{x}_1, \bar{y}_1)}} \overline{A(\bar{x}_1, y_2)} \bar{y}_1.$$

We suppose that the functional $A(x, y)$ is non-degenerate, i. e. if $A(x, y) = 0$ for every $x(y)$, then $y = 0$ ($x = 0$).

Further in (9) we set

$$(19) \quad d_k = A(\bar{x}_k, \bar{y}_k) \quad u_{ki} = A(x_k, \bar{y}_i), \quad v_{ki} = A(\bar{x}_i, y_k).$$

Then (8) here means

$$(20) \quad x_k = \sum_{i=1}^k b_{ki} \bar{x}_i \quad \text{and} \quad y_k = \sum_{i=1}^k \bar{c}_{ki} \bar{y}_i,$$

where the coefficients are defined by (9) and by recurrent formulas (10), in which we put $a_{kj} = A(x_j, y_k)$. The transformation (20) define the canonical bases (x_k) , (y_k) , i. e. $A(\bar{x}_k, \bar{y}_j) = 0$ for $k \neq j$.

Thus, if $x = \sum_{i=1}^n a_i \bar{x}_i$ and $y = \sum_{i=1}^n \beta_i \bar{y}_i$ then $A(x, y) = \sum_{i=1}^n d_i a_i \bar{\beta}_i$.

Formulas (12), (13) and (14) are also valid in this case.

3. Let us assume that $Y=X$ and $y_k=x_k$ for $k=1,2,\dots,n$.

In this case the transformations (20) are of the form

$$(21) \quad x_k = \sum_{i=1}^k b_{ki} \bar{x}_i \quad \text{and} \quad x_k = \sum_{i=1}^k \bar{c}_{ki} \bar{y}_i.$$

Thus we obtain a canonical form for $A(x,y)$ relative to two canonical bases (x_i) and (y_i) in X ; all the assertions of 2 remain true.

4. Now let us assume that $A(x,y)$ is a Hermitian bilinear form on the Cartesian product $X \times X$, i. e. $A(x,y) = \overline{A(y,x)}$ for every $x,y \in X$. Let (x_k) , $k=1,2,\dots,n$ be a basis in X . Let us write the transformations (21). By (19) and (20) we have

$$(22) \quad \begin{cases} \bar{x}_1 = x_1 & \bar{y}_1 = y_1 = x_1 \\ \bar{x}_k = x_k - \sum_{i=1}^{k-1} \frac{1}{\bar{d}_i} u_{ki} \bar{x}_i & \text{and} \quad y_k = x_k - \sum_{i=1}^{k-1} \frac{1}{\bar{d}_i} \bar{v}_{ki} \bar{y}_i, \end{cases}$$

where $u_{ki} = A(x_k, \bar{y}_i)$, $v_{ki} = A(\bar{x}_i, x_k)$ by (19).

Since $\bar{d}_1 = A(\bar{x}_1, \bar{x}_1)$ is real and $u_{ki} = A(x_k, \bar{y}_i) = A(x_k, \bar{x}_i) = \overline{A(\bar{x}_i, x_k)} = \bar{v}_{ki}$ we get by (10) $v_{kj} = \bar{u}_{kj}$ and $\bar{c}_{ki} = b_{ki}$ by (9).

Thus by (22) we have $\bar{y}_k = \bar{x}_k$ ($k=1,2,\dots,n$) i. e. the canonical bases coincide, forming one canonical basis.

Recurrent formulas (10) should be written as follows

$$(23) \quad \begin{cases} u_{kj} = a_{jk} - \sum_{i=1}^{j-1} \frac{1}{\bar{d}_i} \bar{u}_{ji} u_{ki}, & a_{jk} = A(x_k, x_j) \\ \bar{d}_k = a_{kk} - \sum_{i=1}^{k-1} \frac{1}{\bar{d}_i} |u_{ki}|^2. \end{cases}$$

By (23) it follows that the numbers \bar{d}_k are real. Equation (13) means

$$(24) \quad A = CDC^* = W^*DW,$$

where $A = \|a_{kj}\|$; $D = \|\bar{d}_i\|$ is the diagonal matrix,

$$C = \|c_{kj}\| = \|\bar{b}_{kj}\| \quad \text{and} \quad W = B' = \|b'_{kj}\|, \quad b'_{kj} = b_{jk}.$$

B is the matrix transforming the basis (x_k) into the canonical basis (\bar{x}_k) by (22).

Equations (13) and (14) show that the method of biorthogonalisation applied to Hermitian bilinear forms coincides with Jacobi's method of reducing to canonical form:

$$A(x,y) = \sum_{i=1}^n \bar{d}_i \xi_i \bar{\eta}_i, \quad \text{where} \quad x = \sum_{i=1}^n \xi_i \bar{x}_i \quad y = \sum_{i=1}^n \eta_i \bar{x}_i,$$

where $\bar{d}_i = A(\bar{x}_i, \bar{x}_i)$ [$A(\bar{x}_k, \bar{x}_i) = 0$ for $k \neq i$].

Evidently it should to be assumed that the principal minors $D_k = A \begin{pmatrix} 1, 2, \dots, k \\ 1, 2, \dots, k \end{pmatrix} \neq 0$ for $k=1, 2, \dots, n$. By (14) we also obtain Jacobi's formula

$$A(x, x) = \sum_{k=1}^n \frac{D_k}{D_{k+1}} \xi_k \bar{\xi}_k \quad (D_0=1).$$

This formula may be regarded as a particular case of a general one for two canonical bases

$$A(x, y) = \sum_{k=1}^n \frac{D_k}{D_{k-1}} \xi_k \bar{\eta}_k,$$

where

$$y = \sum_{k=1}^n \eta_k \bar{y}_k, \quad x = \sum_{k=1}^n \xi_k \bar{x}_k.$$

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A Generalisation of Stone's Theorem on Approximation

by

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Presented by S. MAZUR on July 18, 1956

This note contains a generalisation of the results of Stone [4], Gelfand and Silov [1] concerning the approximation of continuous functions, defined in a bicomact topological space, to the case of continuous functions with values from a space of type B_0^* .

Consider a space $C_E(P)$ of continuous functions x, y, \dots defined in a bicomact Hausdorff topological space P with values from a certain space E of type B_0 .

Suppose we are given a family of functions $(x_\alpha) \subset C_E(P)$ (the index α running over a certain abstract set \mathfrak{A}).

Definition 1. Family (x_α) divides the points p_1 and p_2 of space P if $\sum_{\alpha \in \mathfrak{A}} [x_\alpha(p_1) \neq x_\alpha(p_2)]$.

Let H be the family of all multilinear operations $A(z_1, z_2, \dots, z_n)$ defined in the space $\underbrace{E^n = E \times E \times \dots \times E}_{n \text{ times}}$, $n = 1, 2, \dots$, with values from space E .

Definition 2. A ring $R(x_\alpha)$ spanned on the family of functions $(x_\alpha) \subset C_E(P)$ is here called the least linear space (closed with respect to the uniform convergence of functions) containing all composed functions of the form $A(x_{\alpha_1}, x_{\alpha_2}, \dots, x_{\alpha_n})$ (where $A \in H$, $\alpha_i \in \mathfrak{A}$, $i = 1, 2, \dots, n$) and all constant functions defined in space P with values from space E .

Note. If we take for E the space of real numbers, then $R(x_\alpha)$ will be the least closed ring containing the family of functions (x_α) .

If we accept this definition of a ring, the theorem of Stone is extended to the case of functions with values from B_0 -spaces; namely we have the following

*) For the definition and basic properties of B_0 -spaces see [3].

**) For the definition and basic properties of multilinear operations see [2].

THEOREM 1. *We are given a family of functions $(x_a) \subset C_E(P)$ and a function $y \in C_E(P)$. In order that $y \in R(x_a)$, it is necessary and sufficient that no pair of points undivided by the family of functions (x_a) be divided by function y .*

The proof of Theorem 1 is based on the following unpublished result of S. Mazur:

(M) *Every continuous operation defined in a compact set Q of space E_1 of type B_0 with values from space E of type B_0 can be uniformly approximated by polynomial operations with arbitrary accuracy.*

If we take for E the space of real numbers R , a slight modification of the proof of Theorem 1 makes it possible to obtain a further strengthening of Stone's theorem.

In order to formulate these results the following notation is introduced (here, symbols x, y denote real functions defined in an arbitrary non-empty set P):

- $$(1) \quad T = \mathcal{G}_{(p_1, p_2) \in P \times P} \left[\prod_{\alpha \in \mathfrak{A}} x_\alpha(p_1) = x_\alpha(p_2) \right],$$
- $$(2) \quad T_{\delta, a_1, a_2, \dots, a_k} = \mathcal{G}_{(p_1, p_2) \in P \times P} \left[\sum_{i=1}^k |x_{a_i}(p_1) - x_{a_i}(p_2)| < \delta \right],$$
- $$(3) \quad \bar{d} = \sup_{(p_1, p_2) \in T} |y(p_1) - y(p_2)|,$$
- $$(4) \quad d = \inf_{\delta > 0, \{a_i, \dots, a_p\} \subset \mathfrak{A}, k=1, 2, \dots} \sup_{(p_1, p_2) \in T} |y(p_1) - y(p_2)|,$$
- $$(5) \quad \varrho(y, R(x_a)) = \inf_{x \in R(x_a)} \sup_{p \in P} |y(p) - x(p)|.$$

THEOREM 2. *Let P be an arbitrary non-empty subset, and $M_R(P)$ — the space of bounded real functions defined on P . Let $(x_a) \subset M_R(P)$ and $y \in M_R(P)$.*

The following formula holds:

$$\varrho(y, R(x_a)) = \frac{1}{2} \bar{d}$$

(the symbol $R(x_a)$ denoting an ordinary closed ring, with the norm $\|x\| = \sup_{p \in P} |x(p)|$, spanned on the family of functions (x_a)).

In the case of P being a bicomact Hausdorff topological space we have the following theorem:

THEOREM 3. *If $(x_a) \subset C_R(P)$; $y \in C_R(P)$, then we have the formula*

$$\varrho(y, R(x_a)) = \frac{1}{2} \bar{d}.$$

Setting $\bar{d} = 0$, we obtain, by formulas (1), (3) and (5), Stone's theorems on approximation.

The proofs will appear in *Studia Mathematica*.

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Elementary Sequences in Almost-Metric Spaces

by

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Presented by K. KURATOWSKI on August 4, 1956

1. Introduction. In functional analysis we generally consider uniform spaces [1] in which uniform topology is given by the set of pseudo norms. In general topology such uniform spaces are called almost-metric spaces [2].

For almost-metric spaces we can introduce the notion of *elementary sequence* (*e-sequence*). The completeness of the space defined by *e*-sequences is equivalent to the usual completeness for uniform spaces [1].

For *e*-sequences we can define the notion of subsequence in the same way as in metric spaces, although this cannot be done in such a simple way for arbitrary Moore-Smith sequences ([3] chap. 2).

In this paper we shall show the connection between total boundedness, bicomactness and certain properties of *e*-sequences of any almost-metric space (Theorem 1 of 3).

Some applications of these considerations will be given in the last paragraph of this paper.

2. Definitions. The set X is called an *almost-metric space with direct set of pseudometrics* if there is a direct set \mathcal{E} of functions $\varrho_\xi(x, y)$ on $X \times X$ such that

- α. $\varrho_\xi(x, y) \leq \varrho_\xi(x, z) + \varrho_\xi(y, z)$ for every $\xi \in \mathcal{E}$ and $x, y, z \in X$,
- β. $x = y$ if, and only if, $\varrho_\xi(x, y) = 0$ for every $\xi \in \mathcal{E}$,
- γ. For every $\xi_1, \xi_2 \in \mathcal{E}$

$$\xi_1 \leq \xi_2 \quad \text{implies} \quad \varrho_{\xi_1}(x, y) \leq \varrho_{\xi_2}(x, y) \quad \text{for any} \quad x, y \in X.$$

Let $\Lambda \stackrel{\text{def}}{=} \mathcal{E} \times N$, where N is the set of natural numbers. We introduce in Λ the relation \leq as follows: for $\lambda_1 = (\xi_1, n_1)$, $\lambda_2 = (\xi_2, n_2)$ we put $\lambda_1 \leq \lambda_2$ if, and only if, $\xi_1 \leq \xi_2$ and $n_1 \leq n_2$.

We introduce a topology in X by a complete family of neighbourhoods

$$U_\lambda(x) = \bigcap_{y \in X} \left(\varrho_\xi(x, y) < \frac{1}{n} \right), \quad \text{where} \quad \lambda = (\xi, n)$$

thus X is a completely regular topological space.

X is also a uniform space [1] with neighbourhoods

$$E_{(x,y) \in X \times X} \left(\varrho_{\xi}(x,y) < \frac{1}{n} \right).$$

Let (x_{λ}) be a function defined on the whole of Λ with values in X . The function (x_{λ}) will be called an e -sequence; (x_{λ}) is called a Cauchy sequence if for every $\lambda = (\xi, n)$ there is a $\mu_{\lambda} \in \Lambda$ such that $\varrho_{\xi}(x_{\lambda'}, x_{\lambda''}) < 1/n$ for $\lambda', \lambda'' \geq \mu_{\lambda}$; the element $x \in X$ is named a *limit* of (x_{λ}) if for every $\lambda = (\xi, n)$ there is a $\mu_{\lambda} \in \Lambda$ such that $\varrho_{\xi}(x, x_{\lambda'}) < 1/n$ for $\lambda' \geq \mu_{\lambda}$. It is easy to see that every e -sequence has at most one limit. Evidently a sequence which has a limit is a Cauchy sequence.

Let (x_{λ}) be an arbitrary e -sequence. Every e -sequence $(x_{\mu_{\lambda}})$, where $\mu_{\lambda} \in \Lambda$ is a function defined on the whole of Λ such that $\mu_{\lambda} \geq \lambda$, is named a sub-sequence of an e -sequence (x_{λ}) .

The space X is called *complete* if every Cauchy e -sequence has a limit. It can be proved that an almost-metric space is complete if, and only if, every Cauchy filter has a limit [1]. Then a complete almost-metric space is a complete uniform space [1].

The space X is called *totally bounded* *) if for every $\lambda = (\xi, n)$ there are $x_1, x_2, \dots, x_k \in X$ such that

$$\min \{ \varrho_{\xi}(x_1, x), \varrho_{\xi}(x_2, x), \dots, \varrho_{\xi}(x_k, x) \} < \frac{1}{n} \quad \text{for } x \in X.$$

3. Fundamental Theorem. We can now formulate a theorem which shows how the notion of bicomcompactness and total boundedness depend on properties of e -sequences.

THEOREM 1. a) *An almost-metric space X is bicomcompact if, and only if, every e -sequence has a convergent sub-sequence.*

b) *The space X is totally bounded if, and only if, every e -sequence has a Cauchy sub-sequence.*

Proof. Given $\xi \in \Xi$ the relation of equivalence in X is defined as follows: $x' \sim x''$ if, and only if, $\varrho_{\xi}(x', x'') = 0$. The equivalence classes and the space of equivalence classes are denoted by $[x]_{\xi}$ and $[X]_{\xi}$ respectively. The space $[X]_{\xi}$ is metric with

$$[\varrho_{\xi}]([x]_{\xi}, [y]_{\xi}) \stackrel{\text{def}}{=} \varrho_{\xi}(x, y).$$

An extension of $[X]_{\xi}$ to a complete metric space is denoted by $[\bar{X}]_{\xi}$.

Let us consider the product space

$$X = P_{\xi \in \Xi} [\bar{X}]_{\xi}$$

and a function $f(x) = \{[x]_{\xi}\}$ which maps homeomorphically X in to X .

*) This notion is equivalent to the precompactness of X in uniform topology, see [1] and [3].

We identify X and $f(X)$. It is easy to prove that $\bar{X} \stackrel{\text{def}}{=} \text{closure } X$ in X is the extension of X to a complete pseudometric space with the same set of extended pseudometrics; $\bar{X} = X$ if, and only if, X is complete. In case X is not totally bounded, there is a $\xi \in \mathcal{E}$ such that $[X]_\xi$ is not, and there is in $[X]_\xi$ a countable sequence $[x_n]_\xi$ which has no Cauchy sub-sequence. It is easy to see that (x_λ) has no Cauchy sub-sequence, where $x_\lambda = x_n$ for $\lambda = (\xi, n)$.

Since the space X is assumed totally bounded, $[X]_\xi$ is also totally bounded and $[\bar{X}]_\xi$ compact. Therefore the space X is bicomcompact [4] and its closed subset \bar{X} is also bicomcompact. The family

$$Z_\eta \stackrel{\text{def}}{=} \bigcup_{X_\eta} (\mu \geq \eta) C \bar{X},$$

where $(x_\lambda) C X$ is an arbitrary e -sequence has a common point. Let $x \in \bigcap_{\eta \in \mathcal{A}} Z_\eta \subset \bar{X}$. Then to every $\lambda = (\xi, n)$ there is a $\mu_\lambda \geq \lambda$ such that

$\rho_\xi(x, X_{\mu_\lambda}) < 1/n$. Therefore $x \in \bar{X}$ is a limit of (x_{μ_λ}) and hence (x_{μ_λ}) is a Cauchy sequence, and thus we have the proof of part b) of Theorem 1.

If the space X is bicomcompact, then $\bar{X} = X$ and the above mentioned sub-sequence (x_{μ_λ}) of (x_λ) has the limit $x \in X$ and thus every e -sequence has a convergent sub-sequence. If, conversely, every e -sequence in X has a convergent sub-sequence then X is complete and totally bounded. Then $X = \bar{X}$ and X is bicomcompact. And thus the proof of Theorem 1 has been established.

4. Applications. At first we give the following well known

COROLLARY 1. *An almost-metric space is bicomcompact if, and only if, it is complete and totally bounded.*

COROLLARY 2. *In a complete almost-metric space the notions of bi-compactness, compactness and quasi-compactness are equivalent.*

Let us consider any linear space U . If we introduce in U a weak topology by giving a set of linear functionals then U is a almost-metric space with the usual pseudometrics (see [5] chap. IV, § 1, Def. 1). It is easy to prove that the notions of boundedness (see [5] chap. III, § 2, Def. 1) and total boundedness of any subset of U are equivalent. Thus we have the following

THEOREM 2. *Let U be a linear space with a given weak topology. Then for bounded subsets of U the notions of completeness and bicomcompactness are equivalent.*

This theorem is closely connected with the results of Alaoglu, Mackey and Eberlein [6].

Another application is the following generalisation of Mazur's theorem [7]:

THEOREM 3. *Let U be a linear topological locally convex space such that every closed bounded subset of U is complete. Then if BCU is totally bounded, the least closed convex set $W \supset B$ is bicomact.*

Proof. It is easy to prove that if B is totally bounded then W is also. Since every totally bounded set is bounded, W is bounded and complete. Hence W is bicomact.

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A Topologisation of the Conjugate Space of a Locally Convex Linear Space

by

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Presented by S. MAZUR on October 23, 1956

1. Introduction. Let X' denote the conjugate space of a locally convex linear topological space X . It is well known that there are such examples of X that X' is an (F') space and not a t -space and is not bornological in the strong topology [1]. In this paper is defined a locally convex topology of X' . This topology is called the *strongest topology* of X' . It is defined in such a way that if X is bornological, then X' is an d -complete bornological t -space and X can be isomorphically imbedded in X'' . The next paper will be devoted to a characterisation of a certain class of Montel-spaces and its connexions with the results of this paper.

2. A characterisation of bornological spaces. DEFINITION 1. Let X be a linear topological locally convex space. We say that X is a *bornological* space if every pseudonorm defined on X and bounded on every bounded subset of X is continuous.

DEFINITION 2. Let X be a linear topological locally convex space. We say that the topology in X can be *decomposed* *) if there exists a family of normed subspaces $X_t([x]_t) \subset X$; $t \in T$ such that

1. X is identical with the least linear space containing X_t .

2. Topology in X is generated by the set of all pseudonorms continuous with respect to each $[x]_t$ separately.

The spaces $X_t([x]_t)$ are named the *decomposition* of the topological space X .

LEMMA 1. *The space X can be decomposed if, and only if, X is bornological.*

DEFINITION 3. A bornological space X is named *d-complete* (decompositionally complete) if X can be decomposed into Banach spaces.

*) It means that X is the inductive limit of normed spaces $X_t([x]_t)$; $t \in T$ (see [1]).

3. A correspondence between bornological and t -spaces. Let X be a locally convex linear topological space.

DEFINITION 4. A symmetric convex set $W \subset X$ is named *absorbing* if for every $x \in X$ there is $\lambda > 0$ such that $\lambda x \in W$; W is named a *barrel* if W is absorbing and closed. We say that X is *t -space* (*espace tonnelé*) if every barrel is a neighbourhood of zero. The following lemmas can be proved:

LEMMA 2. X is t -space if, and only if, every family \mathcal{G} of continuous linear functionals on X bounded in every point of X separately is a family of equicontinuous functionals.

From Lemmas 1 and 2 we obtain

LEMMA 3. Every d -complete bornological space is t -space.

4. The strongest topology in conjugate space. DEFINITION 5. Let X be a linear topological locally convex space. A family \mathfrak{R} of subsets of X will be called *bounded* if for every $U \subset X$ which is a neighbourhood of zero there is a real number $\lambda > 0$ and an element $A \in \mathfrak{R}$ such that $\lambda A \subset U$.

DEFINITION 6. Let X' be the conjugate space of the linear topological locally convex space X and let us consider in X' the pseudonorms:

$$|x'|_{\mathfrak{R}} = \inf_{A \in \mathfrak{R}} \left(\sup_{x \in A} x'(x) \right),$$

where $x'(x)$ denotes the value of $x' \in X'$ on the element $x \in X$ and \mathfrak{R} is a bounded family of nonvoid convex symmetric subsets of X , such that for every $A, B \in \mathfrak{R}$ there is $C \in \mathfrak{R}$ such that $CC \subset A \cap B$.

The topology induced in X' by pseudonorms $|x'|_{\mathfrak{R}}$ will be named the *strongest topology* of conjugate space.

THEOREM 1. Let X be a locally convex linear topological space with pseudonorms $|x|_{\omega}$, $\omega \in \Omega$. Let us denote by X'_{ω} the subspace of X' which consists of all functionals continuous with respect to $|x|_{\omega}$. If we introduce in X'_{ω} the norm

$$[x']_{\omega} = \sup_{|x|_{\omega} \leq 1} x'(x)$$

then the spaces $X'_{\omega}([x]_{\omega})$ determine a decomposition of the space X' in the strongest topology.

And so from Lemma 1 we obtain

THEOREM 2. The conjugate space with the strongest topology is a d -complete bornological space.

From Lemma 3 and Theorem 2 we obtain the following

COROLLARY 1. The conjugate space with the strongest topology is a t -space.

Let X'' be the conjugate to X' in the strongest topology. We shall denote by $x''(x')$ the value of $x'' \in X''$ on $x' \in X'$. Then we have the following

THEOREM 3. The mapping $F(x) = x'_{(x)}$, where $x'_{(x)}(x') \stackrel{\text{def}}{=} x'(x)$ for every $x' \in X'$ is the one-to-one imbedding of X into X'' , and

1. F^{-1} is continuous,
2. F maps bounded sets of X onto bounded sets of X'' .

COROLLARY 2. If X is a bornological space then F is bicontinuous.

THEOREM 4. A pseudonorm defined on conjugate space of an arbitrary bornological space is continuous in strongest topology if, and only if, it is bounded in strong topology.

(The strong topology in X' is introduced by the set of pseudonorms $|x'|_B = \sup_{x \in B} |x'(x)|$, where B runs over the set of all bounded subsets of X , see [1]).

THEOREM 5. A one-to-one mapping $f(x') = x'$ of X' in strongest topology onto X' in strong topology is continuous. If X is bornological then the mapping f is bicontinuous if, and only if, X' is a bornological space in the strong topology.

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Applications quasi-monotones et revêtements

par

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Nous donnons ici un théorème qui permet de décrire le comportement du groupe fondamental par rapport à certaines applications quasi-monotones et aussi un exemple d'espace univoherent à revêtement fini multivoherent.

1. X étant un espace topologique connexe et localement connexe (c. l. c.), on dit ([1] p. 40) que (\tilde{X}, f) est un revêtement de X si $f: \tilde{X} \rightarrow X$ est continue et telle que tout $x \in X$ possède un voisinage ouvert revêtu (evenly covered). On dit que $UC X$ est revêtu (par (\tilde{X}, f)) si f applique topologiquement chaque composante de $f^{-1}(U)$ sur U . $\tilde{G}(X, f)$ désigne le groupe des homéomorphismes ξ de \tilde{X} sur \tilde{X} tels que $f_0 \xi = \xi$ (Deckbewegungsgruppe). (\tilde{X}, f) est régulier, si $f(\tilde{x}_1) = f(\tilde{x}_2)$, $\tilde{x}_1, \tilde{x}_2 \in \tilde{X}$ implique $\tilde{x}_2 = \xi(\tilde{x}_1)$, $\xi \in G(\tilde{X}, f)$. Si \tilde{X} est simplement connexe au sens de ([1], p. 44) *), nous posons $G(\tilde{X}, f) = \tilde{\pi}_1(X)$. On sait que si $\pi_1(\tilde{X}, \tilde{x}_0) = 0$ **), alors $\tilde{\pi}_1(X) \approx \pi_1(X, x_0)$.

Soit Y c. l. c.; soit (\tilde{Y}, g) un revêtement régulier de Y et $\varphi: X \rightarrow Y$ continue; soit $\tilde{\varphi}: \tilde{X} \rightarrow \tilde{Y}$ continue et telle que $\varphi \circ f = g \circ \tilde{\varphi}$. Il existe alors pour tout $\xi \in G(\tilde{X}, f)$ un $\eta \in G(\tilde{Y}, g)$ unique, tel que $\tilde{\varphi} \circ \xi = \eta \circ \tilde{\varphi}$ et $\eta = \Phi(\xi)$ définit un homomorphisme Φ de $G(\tilde{X}, f)$ dans $G(\tilde{Y}, g)$, qu'on appelle induit par φ ([2] lemme 4.1). Deux homomorphismes induits par φ différent par un automorphisme intérieur de $G(\tilde{X}, f)$. Enfin on peut montrer que si $\pi_1(X)$ et $\pi_1(Y)$ sont isomorphes à $\pi_1(X, x_0)$ et $\pi_1(Y, y_0)$, Φ peut être identifié à l'homomorphisme de $\pi_1(X, x_0)$ dans $\pi_1(Y, y_0)$ induit par φ qu'on définit classiquement.

*) C'est-à-dire si tout revêtement de \tilde{X} est trivial.

**) $\pi_1(\tilde{X}, \tilde{x}_0)$ désigne le groupe fondamental de \tilde{X} avec le point base \tilde{x}_0 .

Dans tout ce qui suit, (\tilde{X}, f) et (\tilde{Y}, g) seront des revêtements réguliers de X et Y , supposés toujours c. l. c.; $\varphi: X \rightarrow Y$ sera une application continue et $\tilde{\varphi}: \tilde{X} \rightarrow \tilde{Y}$ une application continue, telle que $\varphi \circ f = g \circ \tilde{\varphi}$.

2. THÉORÈME. *Si l'on a*

$$1) \quad \tilde{\varphi}(\tilde{X}) = \tilde{Y}$$

et s'il existe un $y \in Y$, tel que

2) $\varphi^{-1}(y)$ est compact, ou bien tel que

2') $\varphi^{-1}(y)$ a un nombre fini de composantes,

alors l'image de l'homomorphisme Φ , induit par φ , est un sousgroupe H de $F(\tilde{Y}, g)$ d'indice fini k .

Démonstration. Soit d'abord $V \subset Y$ un ouvert connexe, soit \tilde{V} une composante de $g^{-1}(V)$ et \tilde{U} une composante de $\tilde{\varphi}^{-1}(\tilde{V})$. Alors $f(\tilde{U})$ coïncide avec une composante de $\varphi^{-1}(V)$. En effet, on a $\varphi(f(\tilde{U})) = g(\tilde{\varphi}(\tilde{U})) \subset V$, donc $f(\tilde{U}) \subset U$, U étant une composante de $\varphi^{-1}(V)$. Soit \tilde{U}_1 la composante de $f^{-1}(U)$ qui contient \tilde{U} . $g(\tilde{\varphi}(\tilde{U}_1)) = \varphi(f(\tilde{U}_1)) \subset V$, donc $\tilde{\varphi}(\tilde{U}_1)$ est contenu dans une composante de $g^{-1}(V)$, qui ne peut être que \tilde{V} , et vu la définition de \tilde{U} , on a $\tilde{U}_1 \subset \tilde{U}$, donc $\tilde{U}_1 = \tilde{U}$. Mais on sait que $f(\tilde{U}_1) = U$ ([1] lemme 5, p. 42), donc $f(\tilde{U}) = U$.

Soient maintenant $y \in Y$ un point qui vérifie 2) ou 2') et $V \ni y$ un ouvert connexe revêtu par (\tilde{Y}, g) . De $\varphi^{-1}(V) \supset \varphi^{-1}(y)$ et de chacune des conditions 2) et 2') il résulte l'existence d'un nombre fini n de composantes U_i et $\varphi^{-1}(V)$, telles que $\bigcup_{i=1}^n U_i \supset \varphi^{-1}(y)$ et que $U_i \cap \varphi^{-1}(y) \neq \emptyset$, $i = 1, \dots, n$. Soit \tilde{V}_0 une composante de $g^{-1}(V)$. Supposons que l'indice du sousgroupe $H \subset G(\tilde{Y}, g)$ est $> n$. On peut alors choisir les éléments $\eta_j \in G(\tilde{Y}, g)$, $j = 0, 1, \dots, n$, $\eta_0 = e$, appartenant à différentes classes d'équivalence à droite par rapport à H . Soit

$$\tilde{y}_0 \in \tilde{V}_0, \quad g(\tilde{y}_0) = y, \quad \tilde{V}_j = \eta_j(\tilde{V}_0), \quad \tilde{y}_j = \eta_j(\tilde{y}_0), \quad \tilde{y}_j \in \tilde{V}_j, \quad j = 0, 1, \dots, n.$$

Désignons par \tilde{U}_j^a , $j = 0, 1, \dots, n$, les composantes de $\tilde{\varphi}^{-1}(\tilde{V}_j)$ telles que $\tilde{U}_j^a \cap \tilde{\varphi}^{-1}(\tilde{y}_j) \neq \emptyset$. La condition 1) ($\tilde{\varphi}(\tilde{X}) = \tilde{Y}$) implique le fait que, pour chaque j , il y a un \tilde{U}_j^a non vide. Les $f(\tilde{U}_j^a)$ étant des composantes de $\varphi^{-1}(V)$, elles coïncident avec certains U_i , $1 \leq i \leq n$. Il en résulte (comme $n+1 > n$) l'existence des indices j_1, j_2 , $0 \leq j_1 < j_2 \leq n$, avec $f(\tilde{U}_{j_1}^a) = f(\tilde{U}_{j_2}^a) = U_{i_0}$. Soit $\tilde{x}_1 \in \tilde{U}_{j_1}^a \cap \tilde{\varphi}^{-1}(\tilde{y}_{j_1})$ et soit $\tilde{x}_2 \in \tilde{U}_{j_2}^a$ avec $f(\tilde{x}_2) = f(\tilde{x}_1)$. (\tilde{X}, f) étant régulier, $\tilde{x}_2 = \xi(x_1)$, $\xi \in G(\tilde{X}, f)$. On a $\tilde{\varphi}(\tilde{x}_1) = \tilde{y}_{j_1}$ et l'on voit aisément que $\tilde{\varphi}(\tilde{x}_2) = \tilde{y}_{j_2}$. Soit $\eta' = \Phi(\xi) \in H$, c.-à-d. $\tilde{\varphi} \circ \xi = \eta' \circ \tilde{\varphi}$. D'une part $\tilde{y}_{j_2} = \eta_{j_2}(\eta_{j_1}^{-1}(\tilde{y}_{j_1}))$ et d'autre part $\eta'(\tilde{y}_{j_1}) = \eta'(\tilde{\varphi}(\tilde{x}_1)) = \tilde{\varphi}(\xi(x_1)) = \tilde{y}_{j_2}$, donc ([4] lemme 1), $\eta_{j_2} \eta_{j_1}^{-1} = \eta' \in H$. Donc, les η_j ne peuvent pas appartenir à de différentes classes par rapport à H , ce qui montre que $k = \text{ind } H \leq n$.

3. On appelle *quasi-monotone* une application continue $\varphi: X \rightarrow Y$, telle que pour tout ouvert connexe VCY , φ applique chaque composante de $\varphi^{-1}(V)$ sur V (cette définition diffère légèrement de celle de ([3] p. 151).

Exemples d'applications quasi-monotones: les applications à la fois ouvertes et fermées (cas particulier: applications ouvertes des espaces compacts), les applications canoniques d'un espace X sur l'espace quotient Y d'un groupe d'homéomorphismes opérant dans X ([4], lemme 4). Si φ est quasi-monotone, on a toujours $\varphi(\tilde{X}) = \tilde{Y}$ ([2] lemme 7.1). D'autre part, si \tilde{X} est simplement connexe, (\tilde{X}, f) est régulier et $\tilde{\varphi}$ existe toujours ([1] p. 50, prop. 1). Donc on a le

COROLLAIRE 1. Si X et Y possèdent des revêtements simplement connexes et si $\varphi: X \rightarrow Y$ est quasi-monotone, vérifiant 2) ou 2'), l'image $\Phi(\tilde{\pi}_1(X)) = H$ est un sousgroupe de $\tilde{\pi}_1(V)$ d'indice fini k .

Citons quelques cas pour lesquels les hypothèses du corollaire 1 sont vérifiées:

- a) X est compact et φ est ouverte;
- b) Y est l'espace quotient d'un groupe compact qui opère dans X , et φ est l'application canonique $\varphi: X \rightarrow Y$;
- c) est monotone *); dans ce cas l'indice $k=1$ et Φ est surjectif ([2], th. 7.4).

4. Voici un exemple qui montre que le corollaire ne s'applique au groupe fondamental $\pi_1(X, x_0)$ que lorsque $\pi_1(X, x_0) \approx \tilde{\pi}_1(X)$. Pour l'obtenir, il suffit de modifier un peu un exemple dû à Griffiths ([5] p. 185), simplifié par R. H. Fox, [9].

Soit A_1 la réunion des circonférences $x^2 - \frac{1}{n}x + y^2 = 0$, $n=1, 2, \dots$ (dans le plan Oxy) et soit A_2 l'ensemble symétrique formé par les circonférences $x^2 + \frac{1}{n}x + y^2 = 0$. Des points $\alpha_1 = (1, 0, 1)$ (resp. $\alpha_2 = (-1, 0, 1)$), $\alpha_1, \alpha_2 \in R^3$ comme sommets, construisons les cônes B_1 (resp. B_2) sur A_1 (resp. A_2). Soit $B = B_1 \cup B_2$. B_1 et B_2 sont contractiles, donc $\pi_1(B_1, 0) = \pi_1(B_2, 0) = 0$ (0 est l'origine de R^3), mais $\pi_1(B, 0)$ possède ([5] 3. 4, p. 186) une infinité de générateurs.

Soit $B_1^*(B_2^*)$ l'ensemble de R^3 obtenu de $B_1(B_2)$ par translation parallèle à Ox , de longueur $+1$ (resp. -1). Soit B^* la réunion de B_1^* , B_2^* et du segment $C = [-1, +1]$ de Ox . Selon un résultat dû aussi à Griffiths ([5], th. 1, p. 176), on a $\pi_1(B_1^* \cup C, 0) = 0$ car C est 1-localement connexe dans $(1, 0, 0)$ et $\pi_1(B_1^*, 0) = 0$, car $B_2^* \cup C$ est aussi 1-localement connexe dans $(-1, 0, 0)$. Soit $\varphi: B^* \rightarrow B$ l'application qui envoie B_1^* et B_2^* identi-

*) Dans le sens de l'équation 6.2 dans [2].

quement sur B_1 et B_2 et C — dans le point 0. φ est monotone, mais $\pi_1(B^*, 0) = 0$, tandis que $\pi_1(B, 0) \neq 0$.

5. On sait que pour X connexe par arcs, le groupe d'homologie singulière aux coefficients entiers $H_1(X)$ est le quotient de $\pi_1(X, x_0)$ par son commutant.

En utilisant cette observation et le corollaire 1, on peut retrouver, dans le cas où $\pi_1 \approx \tilde{\pi}_1$ un résultat connu de Eilenberg ([6], th. 10) et de Whyburn [7], qui l'énoncent pour X compact mais sans imposer à X des conditions locales.

COROLLAIRE 2. *Dans les hypothèses du corollaire 1, si $\pi_1(X, x_0) \approx \tilde{\pi}_1(X)$, $\pi_1(Y, y_0) \approx \tilde{\pi}_1(Y)$ (par exemple pour X et Y localement simplement connexes), l'homomorphisme $\varphi_*: H_1(X) \rightarrow H_1(Y)$ induit par φ a comme image un sousgroupe de $H_1(Y)$ d'indice fini k (si φ est monotone, $k=1$). Si les nombres de Betti sont définis, $b_1(X) \geq b_1(Y)$.*

6. Si X et Y sont c. l. c. et $\varphi: X \rightarrow Y$ est quasi-monotone, et $\varphi^{-1}(y_0)$, $y_0 \in Y$ est compact ou à un nombre fini de composantes, alors $r(X) \geq r(Y)^*$. L'exemple suivant montre que $r(X) \geq r(Y)$ peut se présenter effectivement dans ces conditions, même si (X, φ) est un revêtement à deux feuillets d'une variété compacte Y de dimension 3.

Soit $X = S^2 \times S^1$ (S^1 est le groupe multiplicatif des nombres $e^{i\theta}$, $\theta \in R^1$); soit $a \rightarrow a^*$, $a \in S^2$ l'involution antipodique. Désignons par $T: X \rightarrow X$ l'involution définie par $T(a, e^{i\theta}) = (a^*, e^{i\theta})$. En identifiant les points x et $T(x)$ on obtient une variété compacte Y . Si $\varphi: X \rightarrow Y$ est la projection canonique, on voit aisément que (X, φ) est un revêtement à deux feuillets de Y .

Soit $\tilde{X} = S^2 \times R^1$; (\tilde{X}, f) avec $f: \tilde{X} \rightarrow X$, $f(a, \theta) = (a, e^{i\theta})$ est évidemment le revêtement universel (simplement connexe) de X . Le groupe $H = G(\tilde{X}, f)$ est formé par les homéomorphismes $(a, \theta) \rightarrow (a, \theta + 2k\pi)$. $(\tilde{X}, \varphi \circ f)$ est le revêtement universel de Y , avec $G(\tilde{X}, \varphi \circ f)$ formé par les homéomorphismes $(a, \theta) \rightarrow (a, \theta + 2k\pi)$ et aussi $(a, \theta) \rightarrow (a^*, -\theta + 2k\pi)$. On vérifie que $G(\tilde{X}, \varphi \circ f)$ n'est pas abélien et que $H \subset G$, $G/H \approx Z_2$ (le groupe cyclique d'ordre 2). H est isomorphe au groupe additif des entiers Z , donc ([8], th. 4), $r(X) = 1$. Pour montrer que $r(Y) = 0$ il suffit de montrer que G n'admet pas Z comme image homomorphe [8].

Soit pour cela K le commutant de G ; Z_2 étant abélien, on a $H \supset K$. Donc (H est cyclique et $K \neq 0$), $H/K \approx Z_q$ cyclique d'ordre q). On a

$$Z_2 \approx G/H \approx (G/K)/(H/K) = (G/K)/Z_q,$$

*) Ceci peut se démontrer soit directement, en adoptant un raisonnement de G. T. Whyburn ([3], 153), soit grâce à notre théorème, en supposant dans ce dernier cas X et Y paracompacts. Comme d'habitude, $r(X)$ désigne $\sup \{b_0(A \cup B)\} - 1$, pour toutes les décompositions $X = A \cup B$, avec A, B fermés et connexes; $b_0(A \cap B)$ désigne le nombre des composantes de $A \cap B$.

donc G/K est un groupe fini. Le dernier résultat montre que toute image homomorphe abélienne de G est finie, donc elle ne peut pas coïncider avec Z .

Nous avons démontré que Y est une variété compacte unicohérente, tandis que X qui revêt Y à deux feuillets (c.-à-d. tout $\varphi^{-1}(y)$, $y \in Y$ contient deux points), est multicohérente.

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On Almost-Metric Spaces

by

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I. We recall that a *pseudometric* is a two-argument non-negative real-valued function ϱ defined on an arbitrary set X and satisfying the following conditions:

1. $\varrho(x, x) = 0$;
2. $\varrho(x, y) = \varrho(y, x)$;
3. $\varrho(x, y) + \varrho(y, z) \geq \varrho(x, z)$.

Let us call *almost-metric space* each set X with a family $P = \{\varrho_\xi\}_{\xi \in E}$ of pseudometrics satisfying the condition

4. If for every $\varrho_\xi \in P$, $\varrho_\xi(x, y) = 0$, then $x = y$.

If the power of the family P is equal to m , then we say that X is an m -almost-metric space.

Let us observe that the family P' consisting of all finite maxima of pseudometrics ϱ_ξ belonging to P has the same power as P and it satisfies the condition

5. For every $\varrho_{\xi_1}, \varrho_{\xi_2} \in P'$ there exists $\varrho_\xi \in P'$ such that $\varrho_\xi(x, y) > \max \{\varrho_{\xi_1}(x, y), \varrho_{\xi_2}(x, y)\}$.

In sequel it will be always assumed that a family of pseudometrics of an almost-metric space satisfies also the condition 5. This condition is only of technical use.

We introduce the topology in an almost-metric space X setting for $A \subset X$, $\bar{A} = \bigcap_{x \in X} \bigcap_{\xi \in E} (\varrho_\xi(x, A) = 0)$ ($\varrho_\xi(x, A)$ denotes the greatest lower bound of the numbers $\varrho_\xi(x, y)$, where $y \in A$). It follows from this definition that X is a completely regular space. Conversely, every completely regular space is homeomorphic to an almost-metric space. Thus almost-metric spaces may be regarded as an instrument for the study of completely regular spaces.

The theory of almost-metric spaces may be developed analogously to the theory of metric spaces; in particular, a generalisation of a notion

of sequence allows us to carry over pseudometric spaces many "sequential" theorems, the importance of which in the theory of metric spaces is well known.

II. Generalisation of the notion of sequence. Let N^m be the weak product of m sets of non-negative integers, i. e., the set of all functions α defined on a set \mathcal{E} of the power m , with non-negative values, and such that $\alpha(\xi) \neq 0$ for a finite number of ξ . The set N^m will be considered as partly ordered, namely, $\alpha \leq \beta$ if $\alpha(\xi) \leq \beta(\xi)$ for every $\xi \in \mathcal{E}$.

A function \mathfrak{X} defined on the set N^m will be called m -sequence. We shall use the common notations and terminology for m -sequences, namely:

if an m -sequence assigns to an element $\alpha \in N^m$ an element x_α , it will be denoted as (x_α) .

if T is a statement on the elements of the set N^m , then we say that T is fulfilled for:

(a) "almost all" $\alpha \in N^m$, if there exists an element $\beta \in N^m$ such that T is fulfilled for every $\alpha \geq \beta$;

(b) "infinitely many" α , if for every $\beta \in N^m$ there exists $\alpha \geq \beta$ such that T is fulfilled for α .

An m -sequence (y_α) is called a subsequence of an m -sequence (x_α) if there exists an m -sequence (β_α) of elements of N^m such that $\beta_\alpha \geq \alpha$ and $y_\alpha = x_{\beta_\alpha}$ for every $\alpha \in N^m$.

An m -sequence (x_α) of elements of a topological space X is said to be convergent to an element $x \in X$ if for every neighbourhood U of x , $x \in U$ for "almost all" α .

III. Some topological properties of almost-metric spaces. If X is an m -almost-metric space then the following statements hold true:

THEOREM 1. Every point $x \in X$ has a basis of neighbourhoods of the power $\leq m$.

THEOREM 2. Every closed set $A \subset X$ is the intersection of m open sets.

THEOREM 3. $x \in \bar{A}$ if, and only if, there exists an m -sequence of elements of A convergent to x .

THEOREM 4. X has a basis of open sets of the power $\leq m$ if, and only if, X contains a dense subset of the power $\leq m$.

THEOREM 5. If X is countably compact (i. e., every open covering of X of the power \aleph_0 contains a finite subcovering), then X contains a dense subset of the power $\leq m$.

THEOREM 6. X is m -compact (i. e., every open covering of X of the power m contains a finite subcovering), if, and only if, X is compact (i. e., every open covering of X contains a finite subcovering).

THEOREM 7. X is compact if, and only if, every m -sequence of elements of X contains a convergent subsequence.

IV. Product of almost-metric spaces. Let $\{X_\eta\}_{\eta \in H}$ be a family of almost-metric spaces and $P_\eta = \{\varrho_\xi^{(\eta)}\}_{\xi \in \mathcal{E}_\eta}$ the family of pseudometrics of the space X_η . We define the family P of pseudometrics of the product $P_\eta X_\eta$ in the following manner: let η_1, \dots, η_k be a finite system of elements of the set H and let $\varrho_{\xi i}^{(\eta)}$ be an arbitrary pseudometric of $H_{\eta i}$. We set for $x, y \in P_\eta X_\eta$

$$\varrho_{\xi_1, \dots, \xi_k}^{(\eta_1, \dots, \eta_k)}(x, y) = \max_{1 \leq i \leq k} \{\varrho_{\xi_i}^{(\eta_i)}(p_{\eta_i}(x), p_{\eta_i}(y))\}.$$

$(p_\eta(x))$ denotes the η -th co-ordinate of the point $x \in P_\eta X_\eta$. The family P consists of all $\varrho_{\xi_1, \dots, \xi_k}^{(\eta_1, \dots, \eta_k)}$.

We see that the topology in $P_\eta X_\eta$ induced by the family P agrees with the ordinary product topology. Hence, by the Tychonoff theorem, we obtain

THEOREM 8. *If X_η are compact almost-metric spaces, then the product $\Pi_\eta X_\eta$ is also compact.*

THEOREM 9. *m-sequence (x_α) of elements of $P_\eta X_\eta$ is convergent to a point $x \in \Pi_\eta X_\eta$ if, and only if, $(p_\eta(x_\alpha))$ converges to $p_\eta(x)$ for every η .*

The above theorems imply the following

THEOREM 10. *Let $\{X_\eta\}_{\eta \in H}$ ($\bar{H} = m$) be a family of compact m-almost-metric spaces. Let there be given for every η an m-sequence $(X_\alpha^{(\eta)})$ of elements of X_η . Then there exists an m-sequence (β_α) of elements of N^m such that $\beta_\eta \geq \alpha$ and $(x_{\beta_\alpha}^{(\eta)})$ is convergent for every η .*

V. m-sequences of sets. Let (A_α) be an m-sequence of subsets of an m-almost-metric space X . We define $Ls A_\alpha$ ($Li A_\alpha$) as the sets of all $x \in X$ such that every neighbourhood of x intersects with "infinitely many" ("almost all") A_α . The sets $Ls A_\alpha$ and $Li A_\alpha$ are closed, and $Li A_\alpha \subset Ls A_\alpha$. Moreover, the equality $Ls A_\alpha = \bigcap_{\beta} \overline{\bigcup_{\alpha \geq \beta} A_\alpha}$ holds. $Ls A_\alpha$ may be also characterised as the set of all $x \in X$ for which there exists an m-sequence (β_α) such that $\beta_\alpha \geq \alpha$ and an m-sequence (x_α) convergent to x such that $x_\alpha \in A_{\beta_\alpha}$. If $Ls A_\alpha = Li A_\alpha$, then the m-sequence (A_α) is said to be convergent and the set $Ls A_\alpha$ is denoted as $\lim A_\alpha$.

The following important statement holds true:

THEOREM 11. *If X is an m-almost-metric space having a dense subset of the power $\leq m$, then every m-sequence of subsets of X contains a convergent subsequence.*

VI. Space 2^X . A subset A of an almost-metric space X is called *bounded* provided that $\sup_{x, y \in A} \varrho_\xi(x, y) < \infty$ for every pseudometric ϱ_ξ of X . The space 2^X is an almost-metric space consisting of all bounded closed

(non-empty) subsets of X with the family $P^* = \{\varrho_\varepsilon^*\}_{\varepsilon \in \mathcal{E}}$ of pseudometrics, where

$$\varrho_\varepsilon^*(A, B) = \max \left\{ \sup_{x \in A} \varrho_\varepsilon(x, B), \sup_{y \in B} \varrho_\varepsilon(A, y) \right\}.$$

The following statement holds true:

THEOREM 12. *If X is a compact m -almost-metric space and (A_α) is an m -sequence of its closed non-empty subsets, then $\lim A_\alpha = A$ if, and only if, $A_\alpha \rightarrow A$ ($A_\alpha \rightarrow A$ means that (A_α) converges to A as an m -sequence of elements of the almost-metric space 2^X).*

If X is a compact almost-metric space, then the topology in 2^X induced by the family P^* of pseudometrics agrees with the topology introduced by Vietoris for regular X . (A basis of the Vietoris topology in 2^X consists of all the sets of the form $\langle U_1, \dots, U_k \rangle$, where U_i are arbitrary open sets of X and $\langle U_1, \dots, U_k \rangle = \mathcal{E} \left(A \subset \sum_i U_i; A \cdot U \neq \emptyset; i=1, \dots, k \right)$.

From Theorems 11 and 12, we obtain at once the following known theorem:

THEOREM 13. *If X is compact then 2^X is also compact.*

VII. Completeness of almost-metric spaces. An m -sequence (x_α) of elements of an almost-metric space is called fundamental if for every pseudometric ϱ_ε in X and every $\varepsilon > 0$ there exists an element $\beta \in N^m$ such that $\varrho_\varepsilon(x_{\alpha'}, x_{\alpha''}) < \varepsilon$ for every $\alpha', \alpha'' \geq \beta$. An m -almost-metric space X is called complete if every fundamental m -sequence of elements of X is convergent to a point $x \in X$.

Let us set $\delta_\varepsilon(A) = \sup_{x, y \in A} \varrho_\varepsilon(x, y)$.

A system \mathfrak{R} of subsets of X is called a Riesz system if for every pseudometric ϱ_ε in X and every $\varepsilon > 0$ there exists $A \in \mathfrak{R}$ such that $\delta_\varepsilon(A) < \varepsilon$.

The Riesz theorem concerning complete metric spaces can be generalised in the following manner:

THEOREM 14. *An almost-metric space X is complete if, and only if, every centred Riesz system of closed subsets of X has a non-empty intersection.*

For every almost-metric space X there exists a complete almost-metric space \tilde{X} which contains X as a dense subset. The method of construction of the space \tilde{X} is the same as that of Hausdorff of a construction of a complete metric space containing a given metric space.

VIII. Space Y^X . A function f defined on an almost-metric space X with the values from an almost-metric space Y is said to be bounded if $\delta_\varepsilon(f(x)) < \infty$ for every pseudometric ϱ_ε in Y . If $P = \{\varrho_\varepsilon\}_{\varepsilon \in \mathcal{E}}$ is a family of pseudometrics of Y , then Y is an almost-metric space consisting of

all bounded continuous functions defined on X with values in Y and with the family $P^* = \{\varrho_\varepsilon^*\}_{\varepsilon \in \Sigma}$ of pseudometrics, where

$$\varrho_\varepsilon^*(f, g) = \sup_{x \in X} \varrho_\varepsilon(f(x), g(x)).$$

The following theorem is a generalisation of the well-known Arzela theorem:

THEOREM 15. *If X and Y are m -almost-metric spaces, X is compact and Y is complete, then the set $CC Y^X$ is compact if, and only if,*

1. *the set $Y_1 = \sum_{f \in C} f(x)$ is compact,*

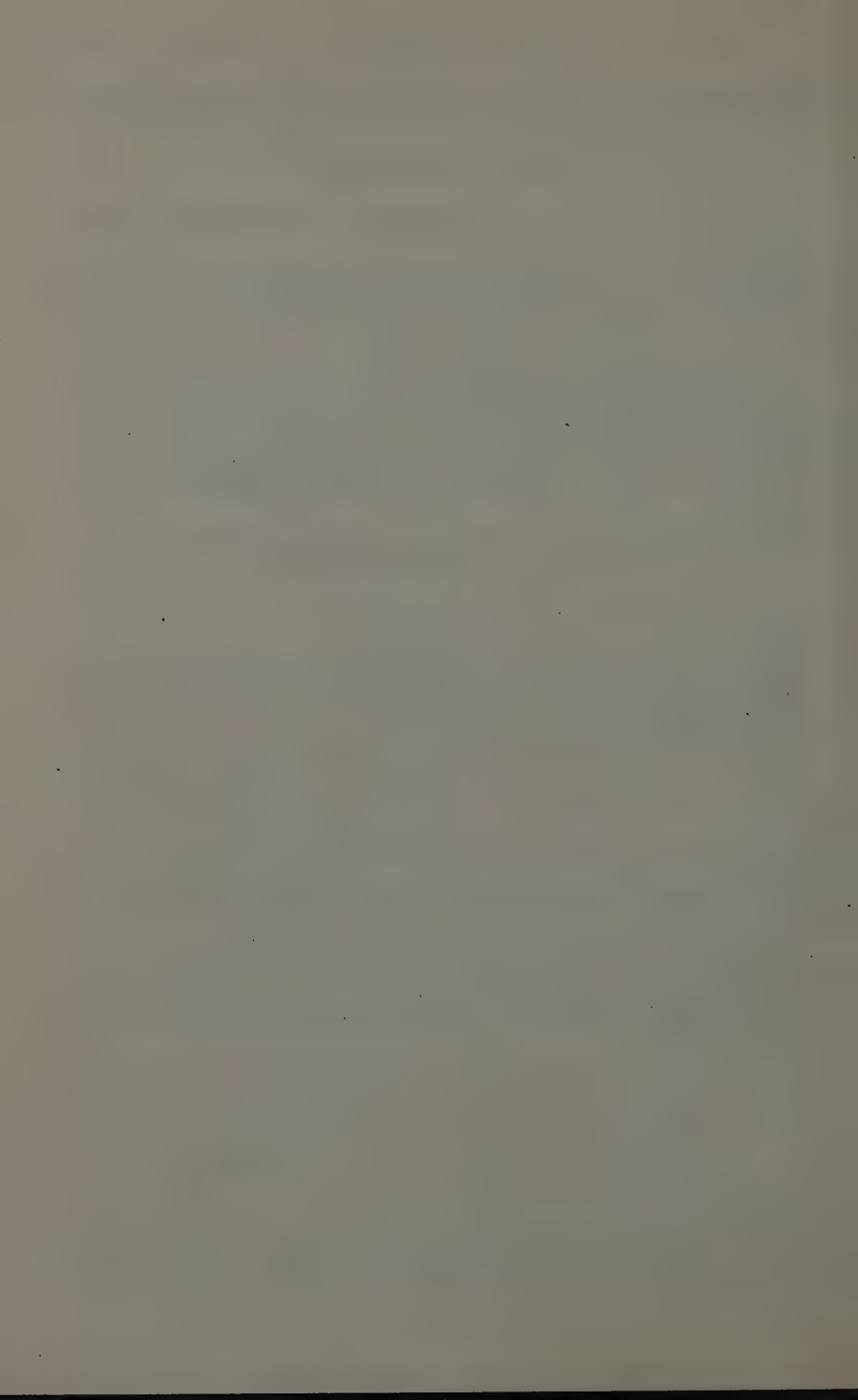
2. *for every $\varepsilon > 0$ and a pseudometric ϱ_ε in Y there exists a number $\delta > 0$ and a pseudometric ϱ'_η in X such that the condition $\varrho'_\eta(x', x'') < \delta$ implies the condition $\varrho_\varepsilon(f(x), f''(x)) < \varepsilon$ for every $x', x'' \in X$ and $f \in C$.*

The proofs of the above theorems will appear in *Fundamenta Mathematicae*.

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Remark on Locally Finite Systems

by

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We recall *) that an almost-metric space is a set X with a family $P = \{\varrho_\xi\}_{\xi \in \Sigma}$ of pseudometrics satisfying the condition

1. if $\varrho_\xi(x, y) = 0$ for every $\varrho_\xi \in P$, then $x = y$.

It may be always assumed (as will be done further on) that a family P of pseudometrics satisfies also the condition

2. for every $\varrho_{\xi_1}, \varrho_{\xi_2} \in P$ there exists $\varrho_\xi \in P$ such that $\varrho_\xi(x, y) \geq \max \{\varrho_{\xi_1}(x, y), \varrho_{\xi_2}(x, y)\}$.

In fact, the family of all maxima of finite numbers of pseudometrics belonging to P satisfies the condition 2, and it has the same power as P .

The topology induced by a family P of pseudometrics is a topology in which the closure operation is defined by the equality $\bar{A} = \bigcap_{x \in X} \bigcap_{\xi \in \Sigma} (\varrho_\xi(x, A) = 0)$ ($\varrho_\xi(x, A)$ being the greatest lower bound of the numbers $\varrho_\xi(x, y)$, where $y \in A$). A topological space X is said to be m -almost-metrisable if it is possible to define a family P of pseudometrics of the power m such that the topology induced by P agrees with the original topology in X . Let us observe that if a space is \aleph_0 -almost-metrisable then it is metrisable; in fact, if $P = \{\varrho_1, \varrho_2, \dots\}$ is a countable family of pseudometrics; then setting

$$\varrho(x, y) = \sum_{i=1}^{\infty} \frac{1}{2^i} \min \{1, \varrho_i(x, y)\}$$

for $x, y \in X$, we obtain a metric such that the topology induced by ϱ agrees with the topology induced by P .

We stated in [2] that, if X is a m -almost-metrisable space, then the following theorems hold true:

*) See [2]. The present paper is closely connected with [2].

- (i) Every point $x \in X$ has a basis of neighbourhoods of the power $\leq m$.
- (ii) Every closed set $A \subset X$ is the intersection of at most m open sets.
- (iii) $x \in \bar{A}$ if, and only if, there exists an m -sequence of elements of A which converges to x .
- (iv) X is m -compact if, and only if, X is compact.
- (v) If X is m -compact then X has an open basis of the power $\leq m$.
- (vi) X is m -compact if, and only if, every m -sequence of elements of X contains a convergent subsequence.

We say that an open basis of a topological space is an m -basis if it is the union of at most m locally finite systems. The general metrisation theorem ([1], p. 127) states that a topological space X is s_0 -almost-metrisable (or, equivalently X is metrisable) if, and only if, X has an s_0 -basis. (X is supposed to be a Hausdorff regular). Thus the problem arises whether the existence of an m -basis is the necessary and sufficient condition for m -almost-metrisability. In this paper it will be shown that this conjecture is valid for normal spaces. Hence, in a normal space having an m -basis, theorems (i)–(vi) hold true. It is not known, whether the existence of an m -basis implies m -almost-metrisability in the case of completely regular space, nevertheless it will be shown that it implies the theorems (i)–(vi).

I. THEOREM 1. *A normal space X is m -almost-metrisable if, and only if, it has an m -basis.*

Proof. The proof is, in fact, the same as that of the general metrisation theorem ([1], p. 128). Let \mathcal{B} be an m -basis and $\mathcal{B} = \sum_{\xi \in \mathcal{E}} \mathcal{B}_\xi$ ($\bar{\mathcal{E}} = m$), where \mathcal{B}_ξ are locally finite systems. For a given ordered pair $\langle \xi_1, \xi_2 \rangle \in \mathcal{E} \times \mathcal{E}$ and for every $U \in \mathcal{B}_{\xi_2}$ we denote by U' the union of all $V \in \mathcal{B}_{\xi_1}$, such that $\bar{V} \subset U$. Since \mathcal{B}_{ξ_1} is locally finite, $\bar{U}' \subset U$, and since X is normal, there exists a continuous function f_U defined on X with values in the unit interval $[0, 1]$, such that $f_U(\bar{U}') = 1$, $f_U(x - U) = 0$. We set $\varrho_{\xi_1, \xi_2}(x, y) = \sum_{U \in \mathcal{B}_{\xi_2}} |f_U(x) - f_U(y)|$. The local finiteness of \mathcal{B}_{ξ_2} implies the continuity of ϱ_{ξ_1, ξ_2} . The family P of all finite maxima of pseudometrics ϱ_{ξ_1, ξ_2} is the required family of pseudometrics.

Conversely, suppose that $P = \{\varrho_\xi\}_{\xi \in \mathcal{E}}$ is a family of pseudometrics of the power m . Let \mathcal{B}_ξ^n be the system of all the sets of the form $\bigcup_{y \in X} E(\varrho_\xi(x, y) < 1/n)$ ($x \in X$), and let $<$ be a relation which well orders the system \mathcal{B}_ξ^n . For every $U \in \mathcal{B}_\xi^n$ and a positive integer k , let

$$U_k = \bigcup_{x \in U} E(\varrho_\xi(x, X - U)) \geq \frac{1}{2^k} \quad \text{and} \quad \tilde{U}_k = U_k - \sum_{U' < U} U'_{k+1}.$$

Obviously, $\varrho_\xi(U_k, X - U_{k+1}) \geq 1/2^{k+1}$ and $\tilde{U}_k \subset U_k \subset U$. Let us observe that if $U' < U$ then $U' \cdot U'_{k+1} = 0$, hence $\tilde{U}_k \subset X - U'_{k+1}$. But $\varrho_\xi(U'_k, X - U'_{k+1}) \geq 1/2^{n+1}$; it follows that $\varrho_\xi(\tilde{U}_k, \tilde{U}_k) \geq 1/2^{k+1}$. For every $U \in \mathfrak{B}_\xi^n$ let

$$\check{U}_k = \bigcap_{x \in X} (\varrho_\xi(x, \check{U}_k)) < \min \left[\frac{1}{n}, \frac{1}{2^{k+3}} \right]$$

and let \mathfrak{B}_ξ^{n+k} be the system of all \check{U}_k . We have [2]:

$$U_k \supset \check{U}_k, \delta_\xi(\check{U}_k) \leq \frac{3}{n} \quad \text{and} \quad \varrho_\xi(\check{U}_k, \check{U}'_k) \geq \frac{1}{2^{k+2}} \quad \text{for every} \\ \check{U}_k, \check{U}'_k \in \mathfrak{B}_\xi^{n,k}, \check{U}_k \neq \check{U}'_k.$$

It follows that the system $\mathfrak{B}_\xi^{n,k}$ is locally finite. We shall show that the union of all $\mathfrak{B}_\xi^{n,k} (\xi \in \mathfrak{E}; n, k = 1, 2, \dots)$ is a basis of X . It suffices to show that for every $x \in X$, $\xi \in \mathfrak{E}$, and a positive integer n there exists a positive integer k and $U \in \mathfrak{B}_\xi^n$ such that $x \in \check{U}_k$. Let U be the first member of \mathfrak{B}_ξ^n which contains x . Then $x \in U_k$ for some k , and for U is the first set containing x , $x \in \check{U}_k$, and finally $x \in \check{U}_k$.

II. Let X be a topological space having an m -basis. We shall show that theorems (i), (iii)–(vi) are valid if X is a Hausdorff space and that the theorem (ii) is valid if X is a regular space. Let \mathfrak{B} be an m -basis of X and let $\mathfrak{B} = \sum_{\xi \in \mathfrak{E}} \mathfrak{B}_\xi (\bar{\mathfrak{E}} = m)$, where \mathfrak{B}_ξ are locally finite systems.

Proof of (i). Let $\mathfrak{M}_\xi(x)$ be the collection of all the members of \mathfrak{B}_ξ which contain x . Since \mathfrak{B}_ξ is locally finite, $\mathfrak{M}_\xi(x)$ is finite and thus the union $\sum_{\xi \in \mathfrak{E}} \mathfrak{M}_\xi(x)$ has the power $\leq m$ and is a basis of neighbourhoods of x .

Proof of (ii). Let $A = \bar{A} \subset X$. Let B_ξ be the set of all points of $X - A$ for which there exists a member $U_x^\xi \in x$ of \mathfrak{B}_ξ such that $A \cdot \bar{U}_x^\xi = 0$. The set

$$G_\xi = \sum_{x \in B_\xi} U_x^\xi$$

is open, and since \mathfrak{B}_ξ is locally finite, $A \cdot \bar{G}_\xi = 0$. Since X is regular and \mathfrak{B} is a basis of X , $X - A = \sum_{\xi \in \mathfrak{E}} \bar{G}_\xi$. Thus, $A = \prod_{\xi \in \mathfrak{E}} (X - \bar{G}_\xi)$.

Proof of (iii). It suffices to show that if $x \in \bar{A}$, then there exists an m -sequence of elements of A convergent to x . Let us assume [2] that an element $\alpha \in N^m$ for which $\alpha(\xi_i) = n_i \neq 0$ ($i = 1, \dots, k$) and $\alpha(\xi) = 0$ for $\xi \neq \xi_i$ will be denoted as $\langle n_1; \xi_1; n_2; \xi_2, \dots, n_k; \xi_k \rangle$. Let \mathfrak{B} be a basis of neighbourhoods of the power m . Set $U_\alpha = U_{\xi_1} \cdot U_{\xi_2} \cdot \dots \cdot U_{\xi_k}$ for $\alpha = \langle n_1; \xi_1; n_2; \xi_2, \dots, n_k; \xi_k \rangle$. Since $x \in \bar{A}$, $A \cdot U_\alpha \neq 0$; we take as u_α an arbitrary element of $A \cdot U_\alpha$. The m -sequence (u_α) is convergent to x .

We shall now show the following lemma:

LEMMA 1. *If X is a Hausdorff m -compact space, then X is normal.*

Proof. At first we shall show that X is regular. Let $x_0 \in A = \bar{A} \subset X$. Denote by A_ξ the set of all points x belonging to A for which there exists a member $U_x^\xi \ni x$ of \mathcal{B}_ξ such that $x_0 \in \bar{U}_x^\xi$. Let $G_\xi = \sum_{x \in A_\xi} U_x^\xi$. Since \mathcal{B}_ξ is locally finite, $x_0 \in \bar{G}_\xi$. Since \mathcal{B} is a basis, $A = \sum_{\xi \in \mathcal{E}} A_\xi$ and therefore $\{G_\xi\}_{\xi \in \mathcal{E}}$ is a covering of A . Since X is m -compact there exists a finite subcovering $\{G_{\xi_1}, G_{\xi_2}, \dots, G_{\xi_k}\}$. Setting

$$G = G_{\xi_1} + G_{\xi_2} + \dots + G_{\xi_k}$$

we see that $x_0 \in \bar{G} \supset G \supset A$ and X is regular. By repeating this reasoning we infer that X is normal.

Proof of (iv). Suppose that X is m -compact. By Lemma 1 X is normal and by Theorem 1 X is m -almost-metrisable, and since (iv) is valid for m -almost-metrisable spaces, X is compact.

Proof of (v). The same as the proof of (iv).

Proof of (vi). It suffices to show that X is m -compact if, and only if, every m -sequence of elements of X contains a convergent sub-sequence. If X is m -compact, then X is m -almost-metrisable and since (iv) is valid for m -almost-metrisable spaces, every m -sequence of elements of X contains a convergent sub-sequence. Suppose that every m -sequence contains a convergent sub-sequence and let $\{F_\xi\}_{\xi \in \mathcal{E}}$, $(\bar{\mathcal{E}} = m)$ be a centred collection of closed sets. Let us write

$$F_\alpha = F_{\xi_1} \cdot F_{\xi_2} \cdot \dots \cdot F_{\xi_k} \quad \text{for} \quad \alpha = \langle n_1; \xi_1, n_2, \xi_2, \dots, n_k; \xi_k \rangle,$$

and let x_α be an arbitrary element of F_α . The m -sequence (x_α) contains a sub-sequence which converges to a point x , and it may be easily proved that x is a common point of all F_ξ ; hence, X is m -compact.

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Continuous Mapping of Subsets of the Euclidean n -Sphere

by

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Introduction

Let A and B be closed subsets of the Euclidean n -sphere

$$S^n = \{x; x \in R^{n+1} \text{ and } \|x\| = 1\}$$

with $A \neq S^n$ and let f be a continuous mapping of A onto B with the following two properties:

- I. $f\{\text{Fr}(A)\}$ and $f\{\text{Int}(A)\}$ are disjoint;
- II. $f|_{\text{Fr}(A)}$ is homeomorphism.

Professor K. Kuratowski has conjectured that $f\{\text{Fr}(A)\} = \text{Fr}(B)$ (hence $f\{\text{Int}(A)\} = \text{Int}(B)$) and has proved his conjecture for the case when $\text{Int}(A)$ is connected. The purpose of this paper is to prove the general case of the conjecture (Theorem 2.4). Since the conjecture is trivial when $n=0$, it will be assumed henceforth that $n \geq 1$.

1. The degree of a continuous mapping

Denote by \mathcal{A} the collection of all triples (h, X, x') , where X is a subset of S^n , h is a continuous mapping of \bar{X} into S^n , and x' is a point of $S^n - h\{\text{Fr}(X)\}$.

It will be assumed that there exists an integral valued function d defined on \mathcal{A} and having the following properties:

- D1. If $(h, X, x') \in \mathcal{A}$, h is the identity mapping of X and $x' \in \text{Int}(X)$, then $d(h, X, x') = 1$.
- D2. If $(h, X, x') \in \mathcal{A}$ and $x' \notin h(\bar{X})$, then $d(h, X, x') = 0$.
- D3. If (h_0, X, x') , $(h_1, X, x') \in \mathcal{A}$ and satisfy the homotopy relation

$$h_0 \sim h_1: \bar{X}, \text{Fr}(X) \rightarrow S^n, S^n - x',$$

then $d(h_0, X, x') = d(h_1, X, x')$.

D4. If X, Y are subsets of S^n with disjoint interiors, h is a continuous mapping of $\bar{X} \cup \bar{Y}$ into S^n and x' is a point of $S^n - h\{\text{Fr}(X) \cup \text{Fr}(Y)\}$, then

$$d(h, X \cup Y, x') = d(h, X, x') + d(h, Y, x').$$

D5. If $(h, X, x') \in \mathcal{A}$ and x'' lies in the same component of $S^n - h\{\text{Fr}(X)\}$ as x' , then $d(h, X, x') = d(h, X, x'')$.

D6. If $(g, Y, y') \in \mathcal{A}$, $X \subseteq S^n$, h is a continuous mapping of \bar{X} into \bar{Y} and $g^{-1}(y')$ is contained in a single component C of $S^n - h\{\text{Fr}(X)\}$, then

$$d(gh, X, y') = d(g, Y, y') \cdot d(h, X, C).$$

(Here $d(f, X, C)$ denotes the constant value of $d(h, X, x)$ for $x \in C$).

This function d can be obtained from the "Abbildungsgrad" of H. Hopf [1] in the following way.

Let $(h, X, x') \in \mathcal{A}$. Since $X \cap f^{-1}(x')$ is compact and is covered by the components of $\text{Int}(X)$, only a finite number C_1, \dots, C_r ($r \geq 0$), of these components will intersect $X \cap f^{-1}(x')$.

(i) If $r = 0$, put $d(h, X, x') = 0$.

(ii) When $r > 0$, $h|C_i$ ($i = 1, \dots, r$) has a "Grad" at x' in the sense of Hopf; put

$$d(h, X, x') = \sum_{i=1}^r (\text{Grad of } h|C_i).$$

The properties D1–D6 now follow immediately from the properties which Hopf established for his Grad.

$d(h, X, x')$ will be called the degree of h on X at x' .

2. The properties of the degree used to prove the Kuratowski conjecture

A, B and f remain the same as in the Introduction. Let p be a point of $S^n - A$ and define a continuous mapping g of S^n into $S^n - p$ by putting

$$g(y) = f^{-1}(y)$$

for $y \in f\{\text{Fr}(A)\}$ and then applying Tietze's Extension Theorem ($S^n - p$ is homeomorphic to R^n) to extend g over S^n (see [3], p. 28 or [2], p. 80).

2.1. THEOREM. Let V be a component of $R^n - \{f\{\text{Fr}(A)\}$ which intersects B , and put $U = f^{-1}(V)$; then

(i) V does not intersect $f\{\text{Fr}(U)\}$, and

$$d(f, U, y) = 0$$

for all $y \in V$;

(ii) $g\{\text{Fr}(V)\}$ does not intersect U or $S^n - \{\bar{U} \cup \text{Fr}(A)\}$ and

$$\begin{aligned} d(g, V, x) &\neq 0 & \text{for } x \in U, \\ &= 0 & \text{for } x \in S^n - \{\bar{U} \cup \text{Fr}(A)\}. \end{aligned}$$

Proof: U and V are evidently open sets of S^n . Also

$$(1) \quad \text{Fr}(U) \subseteq \text{Fr}(A),$$

because otherwise there would exist a point $a \in \text{Fr}(U)$ with $a \in \text{Int}(A)$; then $f(a) \notin f\{\text{Fr}(A)\}$ and, since $f(a) \in \bar{V}$, $f(a) \in V$, $a \in U$; a contradiction.

By (1), V does not intersect $f\{\text{Fr}(U)\}$. Since $\text{Fr}(V) \subseteq f\{\text{Fr}(A)\}$, one has $g\{\text{Fr}(V)\} \subseteq f^{-1}[f\{\text{Fr}(A)\}] = \text{Fr}(A)$ which does not intersect U or $S^n - \{\bar{U} \cup \text{Fr}(A)\}$.

Let x be an arbitrary point of $U \cup [S^n - \{\bar{U} \cup \text{Fr}(A)\}]$ and y an arbitrary point of V . Then $\bar{V} \cap g^{-1}(x) \subseteq V$, hence by D6,

$$(2) \quad d(gf, U, x) = d(g, V, x) \cdot d(f, U, y).$$

Denote the identity mapping of \bar{U} by η . It follows from (1), that $gf(u) = \eta(u)$ for all $u \in \text{Fr}(U)$; hence, since $gf(\bar{U})$ and $\eta(\bar{U})$ are both contained in $S^n - p$, there exists a homotopy relation:

$$gf \sim \eta: \bar{U}, \text{Fr}(U) \rightarrow S^n, S^n - x.$$

Therefore by D3, $d(gf, U, x) = d(\eta, U, x)$ and by D1 and D2,

$$(3) \quad d(gf, U, x) = 1 \text{ or } 0,$$

according as $x \in U$ or $S^n - \{\bar{U} \cup \text{Fr}(A)\}$. Since U is non-empty, it follows from (2) and (3) that

$$(4) \quad d(f, U, y) \neq 0$$

for all $y \in V$. It now follows from (2), (3), and (4) that

$$d(g, V, x) \neq 0 \text{ or } = 0,$$

according as $x \in U$ or $S^n - \{\bar{U} \cup \text{Fr}(A)\}$.

2.2. LEMMA.

$$\text{Fr}(B) \subseteq f\{\text{Fr}(A)\}^*.$$

Proof. Suppose the lemma is not true. There exists a point $b \in \text{Fr}(B)$ with $b \notin f\{\text{Fr}(A)\}$. Let V be the component of $S^n - f\{\text{Fr}(A)\}$ containing b and put $U = f^{-1}(V)$. By Theorem 2.1, $d(f, U, y) = 0$ for all $y \in V$. But since V is open and $b \in \text{Fr}(B)$, V must contain a point $b' \notin B$, hence $b \notin f(\bar{U})$, so that by D2, $d(f, U, b') = 0$. A contradiction.

*) It has been pointed out by A. Kosiński that Lemma 2.2 can also be proved by showing that f is extinguishing on $\text{Int}(A)$ and then applying K. A. Sitnikov [4], p. 439, Theorem 1.

2.3. LEMMA.

$$\begin{aligned} d(g, B, x) &\neq 0 & \text{for } x \in \text{Int } A \\ &= 0 & \text{for } x \in S^n - A. \end{aligned}$$

(Note: It follows from Lemma 2.3, that $g\{\text{Fr}(B)\} \subseteq \text{Fr}(A)$).

Proof. Let $x \in S^n - \text{Fr}(A)$, and put

$$\begin{aligned} G &= \{B \cap g^{-1}(x)\} \cup fx & \text{if } x \in \text{Int } A \\ &= B \cap g^{-1}(x) & \text{if } x \in A. \end{aligned}$$

If G is empty, then $x \notin A$ and also $x \notin g(B)$, so that by D2, $d(g, B, x) = 0$. Hence, one can assume that G is not empty. Denote by \mathcal{V} the collection of those components of $S^n - f\{\text{Fr}(A)\}$ that are contained in B . By Lemma 2.2.,

$$B - f\{\text{Fr}(A)\} = \bigcup_{V \in \mathcal{V}} V.$$

G is compact and is contained in $B - f\{\text{Fr}(A)\}$; therefore, since the sets of \mathcal{V} are open, at most a finite number

$$V_1, \dots, V_r \quad r \geq 1$$

of them intersect G . Put

$$V_0 = B - \bigcup_{i=1}^r V_i,$$

whence by D4,

$$d(g, B, x) = \sum_{i=0}^r d(g, V_i, x),$$

and by D2,

$$(1) \quad d(g, B, x) = \sum_{i=1}^r d(g, V_i, x).$$

Put

$$U_i = f^{-1}(V_i) \quad i = 1, \dots, r.$$

If $x \notin A$, then by Theorem 2.1, $d(g, V_i, x) = 0$ for each i so that, by (1),

$$d(g, B, x) = 0.$$

If $x \in \text{Int } A$, then it belongs to just one U_i — say $U_{i'}$. By Theorem 2.1,

$$\begin{aligned} d(g, V_i, x) &\neq 0 & \text{for } i = i' \\ &= 0 & \text{for } i \neq i'. \end{aligned}$$

Hence by (1),

$$d(g, B, x) \neq 0.$$

2.4. THEOREM

$$f\{\text{Fr}(A)\} = \text{Fr}(B).$$

Proof. Because of Lemma 2.2, it remains only to prove that $f\{\text{Fr}(A)\} \subseteq \text{Fr}(B)$. Suppose this inequality is not true. There exists a point $b \in f\{\text{Fr}(A)\}$ with $b \notin \text{Fr}(B)$. Put

$$a = g(b) = f^{-1}(b).$$

Then $a \in \text{Fr}(A)$ and $b \in \text{Int}(B)$.

(i) If $a \in \overline{\text{Int}(A)}$. Since $a \notin f^{-1}\{\text{Fr}(B)\} = g\{\text{Fr}(B)\}$, there exist points a', a'' in the same component of $S^n - g\{\text{Fr}(B)\}$ with $a' \in \text{Int}(A)$, $a'' \in S^n - A$. By D5,

$$d(g, B, a') = d(g, B, a'')$$

and this contradicts Lemma 2.3.

(ii) If $a \notin \overline{\text{Int}(A)}$. One has $b \notin f\{\text{Int}(A)\}$. Since $b \in \text{Int}(B)$, there exists an open spherical neighbourhood E of b with $E \subseteq \text{Int}(B)$ and \bar{E} not intersecting $f\{\overline{\text{Int}(A)}\}$. Then $\bar{E} \subseteq f\{\text{Fr}(A)\}$ and f^{-1}/\bar{E} is a homeomorphism. Therefore, by Lemma 2.2,

$$\text{Fr}\{f^{-1}(\bar{E})\} \subseteq f^{-1}\{\text{Fr}(\bar{E})\},$$

so that $a \notin \text{Fr}\{f^{-1}(\bar{E})\}$ and hence $a \in \text{Int}\{f^{-1}(\bar{E})\}$, $a \in \text{Int}(A)$; a contradiction.

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Invariante Metriken in homogenen Räumen

von

A. GOETZ

Vorgelegt von A. MOSTOWSKI am 13 December 1956

Wir betrachten einen topologischen Raum \mathcal{M} , in dem eine topologische Gruppe G von homöomorphen Transformationen transitiv so wirkt, dass die Funktion xP ($x \in G$, $P \in \mathcal{M}$) stetig in den beiden Veränderlichen ist und die Abbildung $x \rightarrow xP$ ($P \in \mathcal{M}$ fixiert) von G auf \mathcal{M} offen ist.

Die Untergruppe, für welche der Punkt P invariant bleibt, bezeichnen wir mit H_P .

Eine Umgebung \mathcal{U} von $P \in \mathcal{M}$ heisst kugelförmig in Bezug auf G , wenn $x\mathcal{U} = \mathcal{U}$ für jedes $x \in H_P$.

SATZ 1. *Eine in Bezug auf G invariante Metrik existiert in \mathcal{M} dann und nur dann, wenn die beiden Bedingungen erfüllt sind:*

(1) *Es existiert ein vollständiges System von kugelförmigen Umgebungen eines willkürlich gewählten Punktes $P_0 \in \mathcal{M}$.*

(2) *Es gilt in \mathcal{M} das erste Abzählbarkeitsaxiom.*

Der Satz ist eine Verallgemeinerung des Kakutanischen Satzes [1] über die Existenz einer linksinvarianten Metrik in topologischen Gruppen mit dem ersten Abzählbarkeitsaxiom, und der Beweis ist eine Modifikation desjenigen von Kakutani.

Aus diesem Satz folgt auch leicht der Satz, den ich in [2] bewiesen habe.

SATZ 2. *Die Bedingung (1) ist notwendig und hinreichend dafür, dass in \mathcal{M} eine in Bezug auf G invariante Struktur *) existiere.*

Dasselbe kann auch folgenderweise ausgesprochen werden:

Die Bedingung (1) ist notwendig und hinreichend dafür, dass in \mathcal{M} eine invariante uniforme Struktur existiere, bei welcher die Transformationen aus G gleichgradig stetig sind.

*) Den Begriff der uniformen Struktur hat A. Weil in [3] eingeführt.

Die Voraussetzung, dass die Abbildung $x \rightarrow xP$ offen ist, ist wesentlich. Dass ohne dieser Voraussetzung der Satz 2 unrichtig ist, kann man an den Beispielen aus [4] ansehen.

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Les sous-groupes purs et leurs duals

par

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Présenté par A. MOSTOWSKI le 11. Décembre 1956

G étant un groupe abélien localement compact G^* désignera le groupe dual, c'est-à-dire le groupe localement compact composé de tous les caractères continus χ de G . Si H est un sous-groupe fermé de G , on a $(G/H)^* = A \subset G^*$, où A (l'annihilateur de H) se compose de tous les χ qui prennent la valeur 1 sur H . Un sous-groupe H de G s'appelle pur, si l'on a

$$nH = H \cap nG$$

pour tout n entier. Nous dirons que le caractère χ d'un groupe G est d'ordre fini n , si $\chi^n \equiv 1$ et si $\chi^m \not\equiv 1$ pour $m < n$. On dira encore que le sous-groupe fermé H de G a la propriété (P), si chaque caractère continu de H d'ordre fini se laisse prolonger sur le groupe G tout entier de façon qu'il y devienne un caractère continu du même ordre.

THÉORÈME 1. *Pour que A soit pur il faut et il suffit que H ait la propriété (P).*

Désignons par K la plus petite classe contenant les groupes engendrés par un entourage compact de l'élément neutre et close par rapport à la relation de dualité. On a les théorèmes suivants:

THÉORÈME 2. *H étant un sous-groupe pur fermé de $G \in K$, l'annihilateur $A = (G/H)^*$ de H est un sous-groupe fermé de G^* .*

THÉORÈME 3. *Pour que le sous-groupe fermé H de $G \in K$ soit pur, il faut et il suffit qu'il jouisse de la propriété (P).*

L'hypothèse $G \in K$ est essentielle dans ces théorèmes.

Les démonstrations des théorèmes 1–3 paraîtront dans *Fundamenta Mathematicae*.

Tetrad Formulation of General Relativity Theory

by

F. A. E. PIRANI

Presented by L. INFELD on November 24, 1956

Many of the difficulties of interpretation of general relativity theory arise from the use of co-ordinate systems to which no exact physical significance is ascribed. One way of avoiding such difficulties is to employ the tetrad formalism. The essential mathematical idea is to introduce at every space-time event an orthonormal tetrad (Vierbein, 4-nuple) *) λ_a^μ , one of which (say, λ_0^μ) is timelike, the other three (λ_a^μ) spacelike. In geometrical terms, the tetrad specifies a local tangent Minkowski space. In physical terms, one interprets λ_0^μ as the 4-velocity of an observer at the event in question, and the λ_a^μ as local Cartesian co-ordinate axes used by that observer at that event.

The difference between this approach and the usual one of choosing a particular co-ordinate system is that instead of supposing that each observer makes measurements relative to the co-ordinate system at large, one assumes that each observer uses a local Cartesian co-ordinate system in his own rest-frame. The results of measurement are just the *physical components* of the corresponding tensors, that is, the scalar products of these tensors with tetrad vectors. These quantities are scalars, depending on the observer's 4-velocity and choice of local Cartesian axes, but not on the space-time co-ordinate system.

The orthogonality relations for the tetrad vectors are

$$(1) \quad \lambda_a^\mu \lambda_{\beta\mu} = \eta_{a\beta}.$$

The inverse matrix to λ_a^μ is $[1] \lambda^\alpha_\mu$ defined by

$$(2) \quad \lambda^\alpha_\mu = \eta^{a\beta} \lambda_{\beta\mu}.$$

*) Greek indices run from 0 to 3, Latin indices from 1 to 3. The letters $a, \beta, \gamma, \epsilon, a, b, c, d, e$ are used as labels for tetrad vectors, the letters $\mu, \nu, \rho, \sigma, m, n, r, s$ as ordinary co-ordinate indices. $c=1$. The Minkowski metric is $\eta_{a\beta} = \eta^{a\beta} = \text{diag}(1, -1, -1, -1)$. A semi-colon denotes the covariant derivative. A subscript 0 is always a tetrad label.

Thus co-ordinate indices are raised and lowered with the metric tensor $g_{\mu\nu}$, $g^{\mu\nu}$ as usual, and tetrad indices with $\eta_{a\beta}$, $\eta^{a\beta}$. Equation (2) implies

$$(3) \quad \lambda^a{}_\mu \lambda_{a\nu} = \eta^{a\beta} \lambda_{a\mu} \lambda_{\beta\nu} = g_{\mu\nu}.$$

The physical components of a tensor, say $A_{\mu\nu}$, are

$$(4) \quad A_{a\beta} = \lambda_a{}^\mu \lambda_\beta{}^\nu A_{\mu\nu}.$$

Thus the physical components of the metric tensor are always $\eta_{a\beta}$.

Interpretation: one can get no physical information from knowledge of the metric tensor at a single space-time event.

Instead of Christoffel symbols, the Ricci rotation coefficients $\gamma_{a\beta\gamma}$ describe deviations from flatness:

$$(5) \quad \gamma_{a\beta\gamma} = -\gamma_{\beta a\gamma} = \lambda_{a\mu;\nu} \lambda_\beta{}^\mu \lambda_\gamma{}^\nu.$$

The physical interpretation of the γ 's, which are scalars, follows from the equation of a geodesic (δ denotes the absolute derivative)

$$(6) \quad \delta v^\mu / \delta \tau = 0,$$

where $v^\mu = dx^\mu/d\tau$ is the unit tangent vector (4-velocity). In terms of physical components, equation (6) reads

$$(7) \quad dv^a/d\tau = \gamma^a{}_{\beta\gamma} v^\beta v^\gamma,$$

where $v^a = \lambda^a{}_\mu v^\mu$ are the physical components of the 4-velocity. Equation (7) is the equation of motion of a (spherically symmetric) test particle, so that $\gamma^a{}_{\beta\gamma} v^\beta v^\gamma$ is the effective gravitational 4-force. In the instantaneous rest-frame of the particle $v^\beta = \delta^\beta_0$, so that $\gamma^a{}_{00}$ is the effective gravitational 3-force.

Now let $\eta^\mu = x'^\mu - x^\mu$ be the infinitesimal orthogonal displacement vector from the world line C of an arbitrary observer to the world-line C' of a neighbouring observer. It can be shown that η^μ satisfies the deviation equation

$$(8) \quad \delta \eta^\mu / \delta \tau = (\lambda^\mu{}_{;\nu} - \lambda^\mu \delta \lambda_\nu / \delta \tau) \eta^\nu.$$

This equation enables one to investigate the way in which neighbouring observers will describe one another's motion. The physical components of (8) are

$$(9) \quad \frac{dX^a}{d\tau} = (\gamma^{ab}{}_0 + \gamma_0{}^{ab}) X_b,$$

where $X^a = \eta^{ab} X_b = \lambda^a{}_\mu \eta^\mu$ are the (non-zero) physical components of the displacement vector. These are just the Cartesian position co-ordinates ascribed by C to C' in the local system used by C (and defined by the $\lambda_a{}^\mu$). The left hand side of (9) is the velocity of C' relative to C .

So far no prescription has been given to relate the axes used by \mathcal{C} at different points of his world-line. These may be chosen arbitrarily and the physical consequences found from equation (9). Let us assume that the axes are propagated by Fermi propagation [2]:

$$(10) \quad (\delta_\nu^\mu - \lambda^\mu \lambda_\nu) \delta \lambda_a^\nu / \delta \tau = 0;$$

then the first term on the right hand side of (9) vanishes. Since γ^{ab}_0 is skew-symmetric in a and b , this term may be interpreted as a rotation term, which is eliminated by this choice of axes.

The acceleration of \mathcal{C}' relative to \mathcal{C} is found by differentiating (9) with respect to τ . In the case that \mathcal{C} and \mathcal{C}' are both geodesics, one obtains the equation of geodesic deviation [3], [4], with physical components

$$(11) \quad \frac{d^2 X^a}{d\tau^2} + K^a_b X^b = 0,$$

where $K^a_b = R^a_{0b0}$ are some of the physical components of the Riemann tensor. Here the space axes are propagated according to (10) which reduces in this case to the equation of parallel propagation. It is known [5] that these equations may be put into Hamiltonian form, whence it follows that the corresponding motion is irrotational.

Equation (11) is identical in form with the equation for the relative acceleration of two particles in a Newtonian gravitational field; in that case K^a_b is just $\partial^2 V / \partial x^a \partial x^b$, where V is the Newtonian potential. This would not be the case if axes other than parallelly propagated axes were used, for then additional terms would appear in (11). Thus in the case of purely gravitating particles, parallel propagation is to be interpreted as connecting the space axes at different points of an observer's world-line in such a way that measurements made relative to these axes are most closely analogous to those made in a Newtonian inertial frame in the Newtonian theory.

By solving equation (11) for a suitable observer in a Schwarzschild space-time, one may easily deduce the de Sitter-Fokker effect [6], [7], namely the inertial drag exerted by the central body on the inertial frame of an observer moving round it. In this effect one may, by considering different observers, distinguish a special relativity kinematical effect (Thomas precession) and a further effect which is an essentially gravitational phenomenon.

To extend the interpretation of the propagation (10) to a non-geodesic world-line, one may consider the spinning test particle of Papapetrou [8]. This is a particle described by a 4-momentum mv^μ and a spin $s^{\mu\nu}$, but the equations found by Papapetrou are three too few to determine the motion. However, if one adjoins to Papapetrou's equations the usual

assumption that the spin-tensor is orthogonal to the 4-velocity:

$$(12) \quad s^{\mu\nu}v_\nu = 0,$$

then his equations become determined and may be reduced to

$$(13) \quad dm/d\tau = 0,$$

$$(14) \quad m\delta v^\mu/\delta\tau - s^{\mu\nu}\delta^2 v_\nu/\delta\tau^2 + \frac{1}{2}R^\mu{}_{\nu\alpha\sigma}v^\nu s^\alpha s^\sigma = 0,$$

$$(15) \quad \delta s^{\mu\nu}/\delta\tau = (v^\mu s^{\nu\sigma} - v^\nu s^{\mu\sigma})\delta v_\sigma/\delta\tau.$$

The first equation shows that the mass of the particle is conserved; the second is the spin-orbit and spin-gravitation interaction equation. The last equation may be understood if one introduces the spin pseudo-vector

$$(16) \quad H^\mu = \frac{1}{2}\eta^{\mu\nu\alpha\sigma}v_\nu s_{\alpha\sigma},$$

where $\eta^{\mu\nu\alpha\sigma}$ is the alternating tensor. In terms of H^μ , (15) may be reduced to

$$(17) \quad (\delta^\mu_\nu - v^\mu v_\nu)\delta H^\nu/\delta\tau = 0,$$

so that the spin pseudo-vector is Fermi-propagated along the world-line of the particle. It follows easily that the spin is of constant magnitude. Thus a spinning test particle will have a fixed spin direction relative to Fermi-propagated axes.

These remarks illustrate the application of the tetrad formalism to derive invariant results in general relativity theory. Fuller details, and applications to the discussion of boundary conditions at a world-tube surface, and to the theory of gravitational waves, will be published elsewhere.

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Le spectre des densités des grandes gerbes du rayonnement cosmique à l'altitude de 230 m

par

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Introduction

Le problème du spectre des densités des grandes gerbes a été étudié par plusieurs auteurs [1]-[9]. Les données expérimentales montrent qu'on peut le représenter sous la forme différentielle suivante:

$$(1) \quad N(\varrho) d\varrho = K\varrho^{-\gamma+1} d\varrho,$$

où N est le nombre des gerbes de densité comprise entre ϱ et $\varrho + d\varrho$, K est une constante dont la valeur dépend de la profondeur du lieu de l'observation dans l'atmosphère, et γ varie lentement en fonction de la densité ϱ .

Il faut pourtant constater que les déterminations de γ faites par différents auteurs ne sont pas concordantes [10]. Les divergences proviennent de la différence entre les méthodes de mesure employées *) et entre les intervalles des densités exploitées. Quelques-uns parmi les auteurs (p. ex. Cocconi [5]) suggèrent une variation de γ en fonction de la densité, les autres (p. ex. Broadbent [6]) constatent l'invariabilité de γ dans un intervalle assez large des densités.

Le présent travail a pour but de résoudre le problème de γ et de trouver d'une façon aussi exacte que possible la fonction $\gamma(\varrho)$.

*) On connaît deux méthodes de mesure de γ , qu'on appelle dans la nomenclature de Cocconi [5] *A* et *B*. *A*. La méthode de variation du rang des coïncidences qui consiste à comparer p. ex. les coïncidences triples aux quadruples entre les systèmes des compteurs de surfaces égales. *B*. La méthode de variation de la surface des compteurs qui consiste à comparer les coïncidences du même ordre entre les systèmes des compteurs dont chacun a changé sa surface dans la même proportion. Pourtant, seule la méthode *B* est correcte parce qu'elle n'exige pas la supposition d'une densité constante moyenne dans toute l'envergure des compteurs et par là même de négliger l'existence du gradient de densité dans la gerbe. Les calculs fondés sur *A* donnent toujours pour γ des valeurs plus élevées que celles obtenues par *B*.

Méthode de mesure et résultats obtenus

On a utilisé la méthode hodoscopique. L'hodoscope était composé de trois systèmes de compteurs GM, chacun comportant 18 compteurs de surfaces S identiques ($S=130 \text{ cm}^2$), placés sous un toit de bois de $2,5 \text{ g/cm}^2$ d'épaisseur. L'enregistrement des coïncidences triples exigeait qu'au moins un compteur dans chacun des systèmes fût actionné. On rapporte tous les enregistrements à un des systèmes de compteurs et c'est ainsi qu'on les divise en 18 classes allant de 1 à 18 compteurs actionnés. On obtient de cette façon trois séries d'enregistrements, dont chacune appartient à un système de compteurs. On a effectué 227.712 enregistrements individuels de ce genre.

En admettant la forme (1) du spectre des densités, on obtient pour la fréquence des enregistrements l'expression suivante:

$$(2) \quad I(m, \gamma) = K \binom{M}{m} \int_0^\infty (1 - e^{-Sp})^m e^{-(M-m)Sp} (1 - e^{-MS\rho})^2 \rho^{-(\gamma+1)} d\rho.$$

M = le nombre total des compteurs compris dans chaque système ($M=18$); m = le nombre des compteurs actionnés.

La solution de (2) est la suivante *):

$$(3) \quad I(m, \gamma) = K \binom{M}{m} S^\gamma \Gamma(-\gamma) (-1)^m \sum_{l=0}^m (-1)^l \binom{m}{l} [(M-l)^\gamma - 2(2M-l)^\gamma + (3M-l)^\gamma],$$

$$(3a) \quad J(m, \gamma) = K S^\gamma \Gamma(-\gamma) P(m, \gamma).$$

On a calculé les valeurs $\Gamma(-\gamma) P(m, \gamma)$ pour m allant de 1 à 18 et pour $\gamma=1,3; 1,4; 1,5; 1,6$. Il s'agit alors de comparer les valeurs expérimentales $p(m)$ avec les valeurs calculées $\Gamma(-\gamma) P(m, \gamma)$. Si l'on admet que $\gamma = \text{Cte}$, la normalisation des valeurs $\Gamma(-\gamma) P(m, \gamma)$ est très simple et consiste à égaliser toutes les sommes $C \sum \Gamma(-\gamma) P(m, \gamma) = \sum p(m)$; on obtient ainsi les constantes de normalisation C pour différents γ . Ce procédé est pourtant inacceptable, si γ varie en fonction de ρ . La normalisation doit se baser dans le cas général sur un procédé ne comprenant aucun postulat *a priori* concernant γ . Une normalisation correcte peut, à notre avis, être effectuée en profitant du fait que les courbes $\Gamma(-\gamma) P(m, \gamma)$ se coupent dans un point commun pour lequel la valeur de $\Gamma(-\gamma) P(m, \gamma)$ ne dépend pas de γ (Fig. 1). Désignons les coordonnées de ce point par $m_0, \Gamma_0 P(m_0)$. On détermine ces valeurs en calculant les quatre paraboles du troisième degré correspondant à $\Gamma(-\gamma) P(m, \gamma)$ pour les valeurs $11 \leq m \leq 14$.

*) Cette solution a été trouvée par M. J. Łopuszański.

Il est commode de se servir de la méthode des moindres carrés dans le but d'obtenir la constante de normalisation C aussi exacte que possible et de mettre à profit l'interdépendance des valeurs $p(m)$ particulières provenant de l'utilisation de l'hodoscope. (La Fig. 2 représente les valeurs $\lg \Phi(m)$ obtenues de cette façon).

On détermine la constante de normalisation en substituant m_0 dans l'équation de $\lg \Phi(m)$; on obtient la valeur de $\Phi(m_0)$ et C . Connaissant C on calcule les valeurs particulières de $\gamma(m)$.

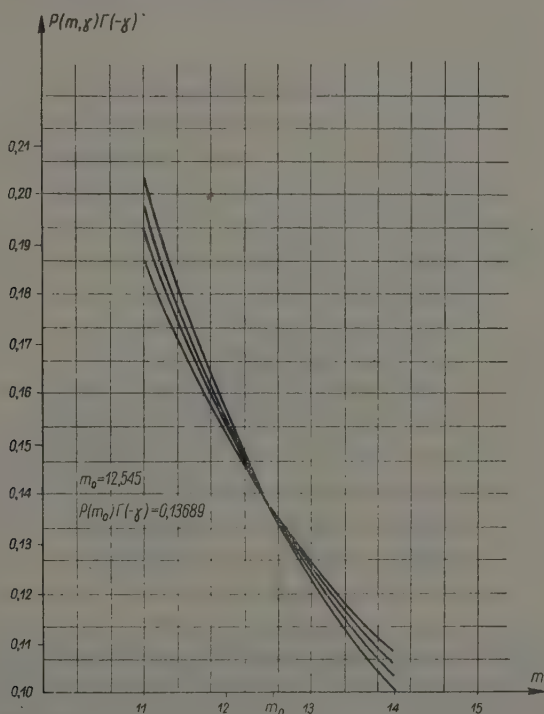


Fig. 1

Il s'agit maintenant de passer de la dépendance $\gamma(m)$ à $\gamma(q)$. Chaque enregistrement m représente un intervalle des densités qui est pratiquement fini. L'intégrande de (2) possédant un maximum accentué, on pouvait profiter de cette circonstance et définir la valeur q_p correspondant au maximum de l'enregistrement (q le plus probable) comme il est adopté p. ex. dans le travail [6]. De l'autre côté, pourtant, la fonction représentant l'intégrande est très asymétrique et pour cette raison \bar{q} (moyenne) est beaucoup plus grande que q_p , p. ex. dans le cas p (1) le rapport $\bar{q}/q_p=3$. Il s'ensuit que la valeur q_p ne représente pas d'une façon convenable l'intervalle des densités définies par un m particulier. Il est pré-

férable d'opérer avec la valeur relative $d\rho/\rho$ au lieu de la valeur $d\rho$ (qui perd d'ailleurs sa signification physique dans un large intervalle de densité). A cet effet on introduit un changement logarithmique de variable ρ

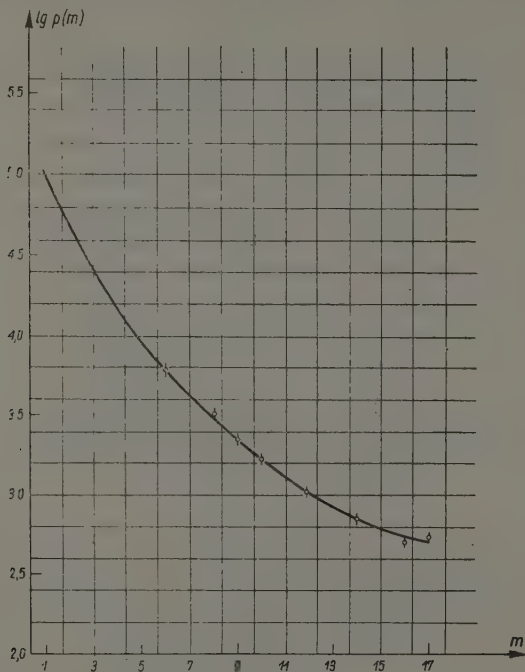


Fig. 2

et de cette façon on symétrise aussi l'intégrande (2). On peut se servir alors de la valeur la plus probable de $\ln \rho$ pour déterminer ρ (ρ logarithmique: ρ_{\ln}) correspondant d'une façon satisfaisante à l'intervalle m donné.

On calcule alors la fonction exprimant la dépendance $\gamma(\rho_{\ln})$ *):

$$(4) \quad \gamma = 1,323 + 0,064 \ln (1 + 0,043 \rho_{\ln}).$$

*) Il est intéressant de noter que le remplacement de la densité moyenne $\bar{\rho}$ par l'inverse de la surface $1/S$, rencontré assez souvent dans la littérature, peut introduire une confusion. En réalité le produit $\bar{\rho}S$ pour une coïncidence triple et $\gamma=1,4$ est égal à 3,2, pour une coïncidence quadruple à 4,4. Par exemple, l'équation de Cocconi [5]:

$$\gamma = 1,310 + 0,038 \ln 1/S \text{ doit s'insérer en termes de } \bar{\rho};$$

$\gamma = 1,296 + 0,027 \ln \bar{\rho}$. On a marqué sur l'axe des abscisses de la figure 3 les valeurs le $\ln 1/S$ et également de $\ln \rho_{\ln}$. En vue de pouvoir comparer d'une façon conventionnelle le résultat du présent travail aux autres résultats on peut l'écrire en utilisant la notation en $1/S$:

$$(4a) \quad \gamma = 1,323 + 0,060 \ln (1 + 0,065 1/S).$$

Contrôle des résultats et calcul des erreurs

Tous les résultats expérimentaux ont été vérifiés au moyen du test χ^2 de Pearson. En particulier on a démontré que les enregistrements hodoscopiques, utilisés pour les calculs, étaient indépendants des facteurs parasites. En se servant des équations normales de la méthode des moindres carrés on a déterminé les erreurs des $\Phi(m)$: $\Delta\Phi(m)$ ainsi que l'erreur commise sur la constante de normalisation C : ΔC . De cette

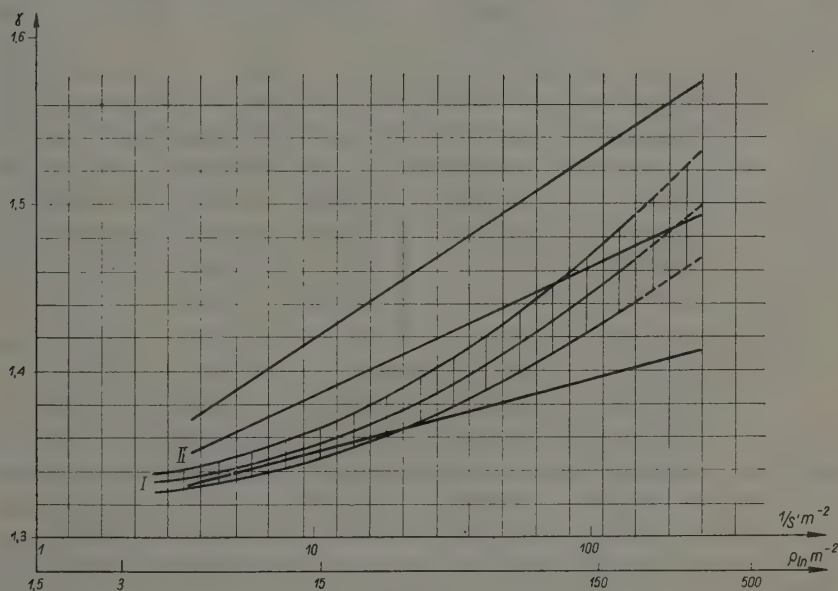


Fig. 3

façon, en utilisant les graphiques d'interpolation pour la fonction $\Gamma(-\gamma)$ $P(m, \gamma)$, on a déterminé les erreurs de γ particuliers.

Les résultats des ces calculs sont représentés à la figure 3. La courbe I reproduit la fonction (4); les deux courbes (inférieure et supérieure) déterminent les limites des erreurs statistiques $\pm \Delta\gamma$ (surface hachurée).

Comparaison avec les résultats antérieurs

I. En appliquant simultanément les méthodes A et B et en utilisant un dispositif de plusieurs compteurs de surfaces différentes travaillant dans une coïncidence triple et quadruple, Cocconi et Cocconi-Tongiorgi [5] ont trouvé la dépendance γ ($1/S$) suivante:

$$(5) \quad \gamma = 1,310 + 0,038 \ln 1/S$$

dans l'intervalle $1/S$ de 2 à 500 m^{-2} .

En vue d'éliminer l'influence de la méthode *A* sur le résultat cité, nous avons répété les calculs en n'utilisant que la méthode *B* étendue à toutes les données expérimentales (y compris les coïncidences quadruples, c'est-à-dire, au total, à 22450 coïncidences divisées en quatre intervalles de densités). Nous avons obtenu la fonction

$$(5a) \quad \gamma = 1,305 + 0,033 \ln 1/S.$$

Cette fonction est représentée à la Fig. 3 (la droite médiane *II*). Les limites des erreurs statistiques sont indiquées par les deux autres droites — l'inférieure et la supérieure.

L'analyse des résultats montre que les données expérimentales de Cocconi pourraient aussi bien s'exprimer par la relation (5a) que par (4a). Par contre, les données expérimentales du présent travail (environ dix fois plus d'enregistrements, divisés en 18 intervalles de densités au lieu de 4) ne peuvent en aucune façon être représentés par la fonction (5a). On peut même démontrer plus généralement *l'impossibilité d'exprimer ces données expérimentales par une fonction quelconque du type $\gamma = a + b \ln 1/S$, à moins que le test χ^2 ne donne une valeur de P plus petite que 0,0001.*

La fonction (5a) de Cocconi est alors une première approximation de la dépendance $\gamma(1/S)$ déterminée par une série restreinte de mesures.

II. Les conclusions de Broadbent et de ses collaborateurs [6], déduites d'une analyse des résultats des mesures hodoscopiques, postulent une valeur constante de γ dans un intervalle des densité compris entre 5 et 500 m⁻². Malgré une analyse minutieuse des données expérimentales, il semble que les auteurs ne pouvaient pas découvrir une variation de γ avec ϱ , d'abord à cause d'une série d'enregistrements trop petite (environ 3000 au total), et puis à cause de la façon de normalisation de leurs résultats qui consiste dans l'égalisation des sommes des polynômes, calculées pour différents γ à une valeur constante, ce qui implique *à priori* une constante de γ .

D'autre part, un des arguments principaux des auteurs, qui contredit la variation de γ , est le suivant: la dispersion totale des résultats, en admettant l'hypothèse $\gamma = \text{Cte}$, est $\Sigma v^2 = 6000$, tandis qu'en admettant la fonction (5a) de Cocconi elle monte à $\Sigma v^2 = 12000$. On peut démontrer pourtant que cette dernière valeur se réduit à 6000 si: 1) on applique la méthode de normalisation par "le point d'intersection"; 2) on utilise ϱ_{in} au lieu de ϱ_p ; 3) on part de la forme différentielle du spectre des densités (1) au lieu de la forme intégrale $N(>\varrho) = B\varrho^{-\gamma}$ de laquelle se servent les auteurs.

III. La valeur moyenne de $\gamma = 1,445 \pm 0,014$, obtenue par Hodson [7] en utilisant l'hodoscope et en calculant par la méthode *B*, est conforme dans les limites des erreurs à la valeur correspondante calculée de la formule (4).

IV. La variation de γ trouvée par Zacepin et ses coll. *) va de 1,35 pour $\varrho=1$ à 1,7 pour $\varrho=10000 \text{ m}^{-2}$ de la formule (4) aux densités $\varrho=10000 \text{ m}^{-2}$.

Je remercie M. Mięsowicz d'avoir prodigué les suggestions et les conseils les plus utiles qui ont grandement contribué au développement du travail; L. Natanson pour l'intérêt dont il a entouré le présent travail; J. Łopuszański pour son apport essentiel dans l'élaboration des fondements théoriques du problème ainsi que pour les maintes discussions, dont j'ai tiré un véritable profit; R. Firkowski pour sa collaboration dévouée, pour son aide incessante dans la surveillance du dispositif expérimental et pour le déchiffrement minutieux de pellicules photographiques.

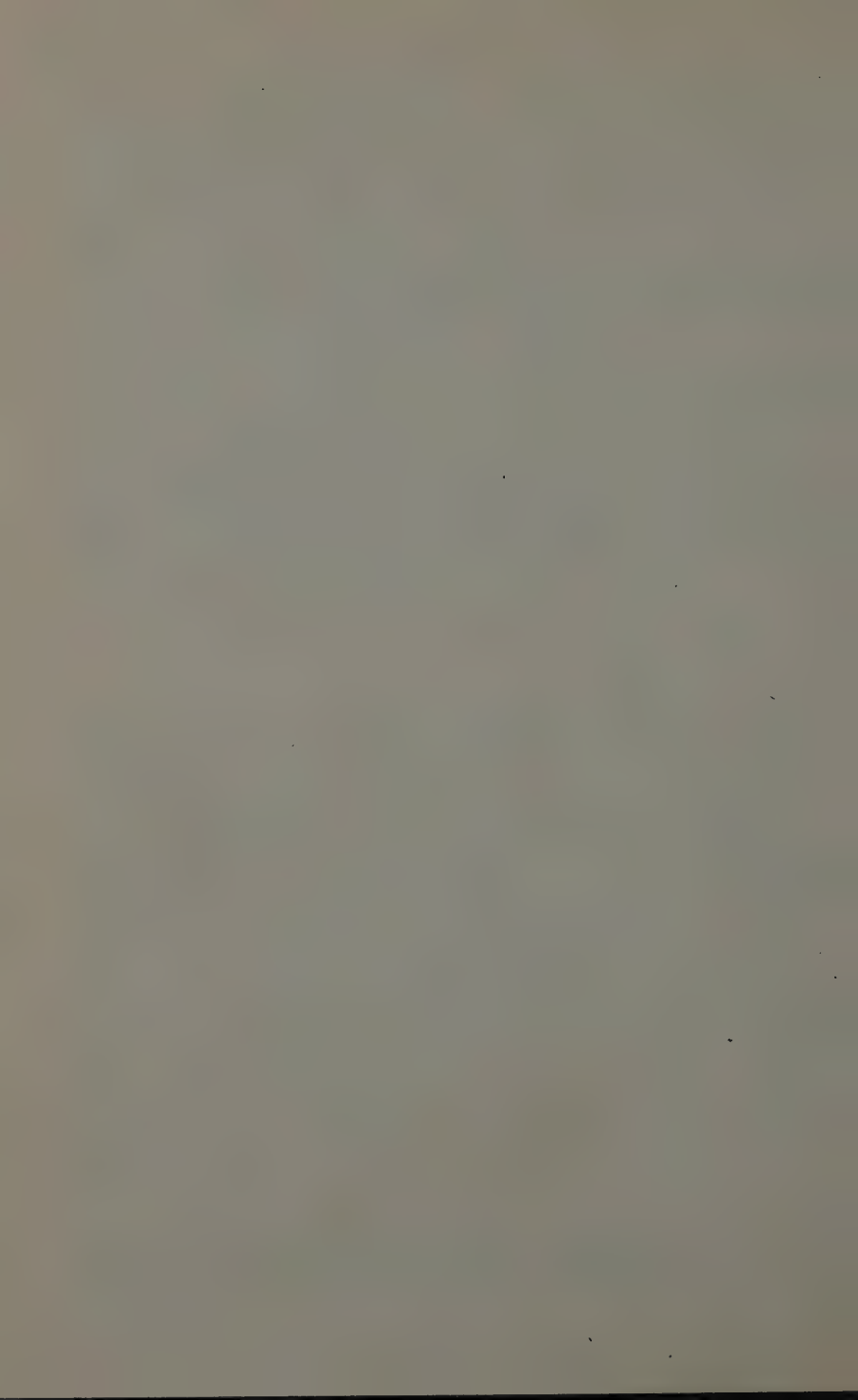
Je tiens également à remercier J. G. Wilson, D. Broadbent et B. D. Hyams de l'Université de Manchester, de m'avoir rendu accessibles tous les détails de leurs installations hodoscopiques dont j'ai profité en grande partie au cours de la construction des appareils; R. Maze et A. Fréon de l'École Normale Supérieure à Paris, pour leurs bienveillants renseignements concernant la technique de la détection des particules.

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*) Les auteurs de [8] et [9] ne donnent aucune dépendance fonctionnelle entre γ et ϱ qui pourrait s'exprimer sous une forme analytique.



Series of Binary Mixtures with Limited Mutual Solubility

by

W. ŚWIĘTOSŁAWSKI and J. STECKI

Presented by W. ŚWIĘTOSŁAWSKI on October 12, 1956

1. General remarks. The transition of homoazeotropes into heteroazeotropes was predicted many years ago by one of the present authors [1]. Recently, a new effort was made to extend this classification [2]. In the meantime interesting experimental investigations were carried out [3], showing a transition of homoazeotropes into zeotropes in (A, H_i) systems, in which A stands for an azeotropic agent, and H_i for one of the representatives of series (H) of homologues. The transition was observed in a single liquid phase, and not at the tie lines which corresponds to two-liquid phase systems.

2. Ideal scheme of binary partially miscible (A, H_i) systems. The (A, H_i) systems, characterised by the partial mutual solubility of the components, usually differ considerably as to the shape of the solubility curves. The variation is so specific for each of the (A, H_i) series, and, in some cases, even for each of the single systems, that a general examination of all series taken together seems to be quite impossible. Therefore, we chose to examine below an ideal case, in which certain simplifications have been introduced.

First of all, we shall here limit ourselves to the cases in which the mutual solubility curves for the whole series of (A, H_i) systems lie close to one another, so that they may be approximatively represented by a single common turbidity curve. Moreover, we do not take into consideration those systems in which the mutual solubility curve, or curves, show a decrease in solubility with the rise of temperature, as, for instance, systems formed by water with certain organic bases. Let us start by presenting Fig. 1 which is similar to that described by one of the present authors [1] many years ago. It represents systems (A, H_i) with one liquid phase only. The importance of the definition of the azeotropic range must be emphasised. In Fig. 1, it is represented by the section $Z_{H_0A_2}$,

of the vertical axis showing the boiling temperatures of the homologues. This section corresponds to the boiling temperatures of all homologues forming azeotropes with agent *A*. Outside the azeotropic range, only homozeotropes are found. If we imagine now that to the diagram

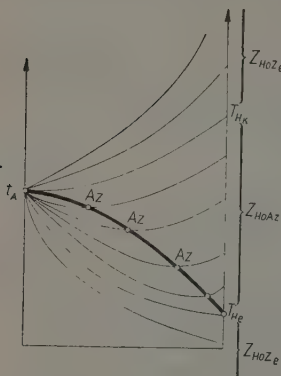


Fig. 1. Scheme showing transition from lower boiling homozeotropes to homoazeotropes, and subsequently to higher boiling homozeotropes.

presented in Fig. 1 a common mutual solubility curve is "built in", then the scheme undergoes certain characteristic changes. Two cases must be distinguished, depending on whether the boiling point t_A of the agent *A* is higher or lower than the critical solubility temperature t_c . The corresponding schemes are shown in Figs. 2 and 3.

Let us examine now the different sections on the axis of temperatures on which the boiling points of homologues are found. If we start from the region of low temperatures, we find the section of heteroazeotropes (*HeZe*) formed by *A* and those homologues which boil lower than t_{He} . Each boiling temperature isobar is characterised by a horizontal section (for instance, *MN*). Starting with point t_{He} , representing the boiling temperature of that homologue which forms with *A* a tangent azeotrope, a new section *HoAz* appears. This corresponds to

boiling temperatures of all representatives lying within the limits from t_{He} to t_{Hp} . If there are many such homologues, then the homoazeotropic points should lie on the curve $t_{He}P$, *P* being the point of intersection with the turbidity line. The boiling temperature isobar of such a system has an azeotropic point outside the horizontal section characterising the two-liquid phase system. If we pass to the next systems. — (*A*, H_{P+1}), (*A*, H_{P+2}) etc. — we find several heteroazeotropes, which are represented by the points *HeAz'*, *HeAz''*, *HeAz'''*, ..., lying on the curve *PQ*, the point *Q* lying on another side of the turbidity curve. The homologues boiling higher than the representative H_Q do form homoazeotropes. In the diagram, the corresponding points are located on the curve t_AQ . The section of homoazeotropes *HoAz* is separated from the heteroazeotropes by point t_{Hk} , representing the boiling temperature of that homologue forming the higher boiling tangent isobar of azeotrope (*A*, H_k).

The scheme shown in Fig. 3 is similar, except that the critical solubility temperature (t_c) is lower than the boiling temperature of the agent (t_A). An essential difference is observed in the upper portion of the drawing only. On certain of the homoazeotropic boiling temperature isobars, the two-liquid horizontal section disappears. The zeotropes formed by higher boiling homologues are typical homozeotropes.

3. Azeotropic ranges of the agent A . In the cases last described, the azeotropic range of agent A in relation to the series (H) is composed of different portions, by contrast with the series of perfectly miscible liquids, forming (A, H_i) homozeotropes and homoazeotropes [4] only. In Figs. 2 and 3, these sections are indicated on axes of temperatures.

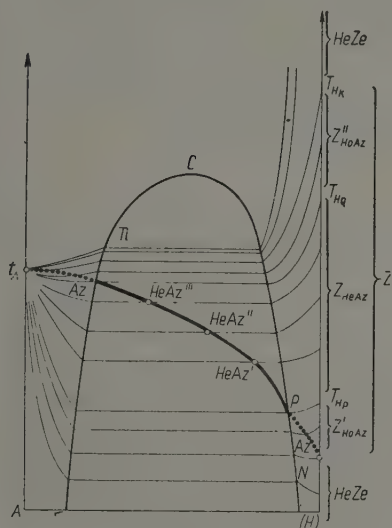


Fig. 2. Scheme showing boiling temperature isobars of an (A, H_i) series. The critical solubility point C lies higher than the boiling temperature of the agent A .

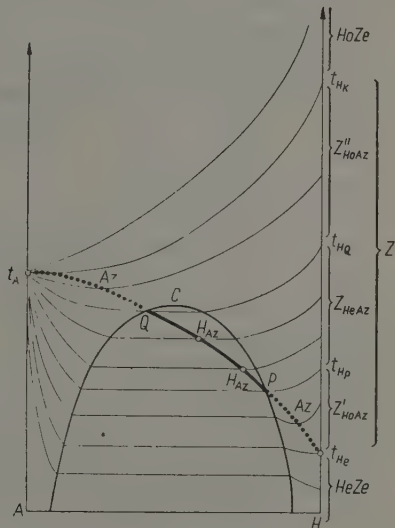


Fig. 3. Scheme showing the boiling temperature isobars for an (A, H_i) series. The critical solubility point C lies below t_A .

Below and above the azeotropic range defined by Eq. (1) only homozeotropes ($HoZe$) and heterozeotropes ($HeZe$) can exist. The azeotropic range is defined, as usual, by the relation:

$$(1) \quad Z_A(H) = t_{H_k} - t_{H_e},$$

in which t_{H_k} and t_{H_e} stand for the boiling temperatures of the respective homologues H_k and H_e , forming with A tangent azeotropes. In the cases examined (Figs. 2 and 3), the formation of homoazeotropes as well as heteroazeotropes may be observed. Consequently, the azeotropic range is composed of three portions: the upper and lower contain homoazeotropes, and that found in the middle — heteroazeotropes. Therefore, we may write:

$$Z_A(H) = Z'_{HoAz} + Z''_{HeAz} + Z'''_{HoAz}.$$

In addition, Z''_{HoAz} may be divided into two parts; in one of them the homoazeotropes lie above the turbidity curve, and in the other, each of the appropriate boiling temperature isobars are characterised by horizontal sections.

4. Deviations from the ideal scheme. After examination of the two ideal schemes, it is easy to predict the kind of deviations which may be encountered in real systems. A simple example is the case in which the critical solubility temperatures of the (A, H_i) systems decrease rapidly with the decrease of the molecular weight of H_i . Consequently, the lower sections, Z'_{HoAz} and Z'_{HeZe} , may disappear entirely.

Recent experiments [5], [3] with two (A, H_i) series confirm the existence of such systems.

It is important to stress a peculiar phenomenon. Each heteroazeotropic point corresponds to the composition of the vapours, which in the course of an isothermal reversible condensation form two liquid phases. The appropriate point is found somewhere inside the turbidity line. If the $HeAz$ curve crosses the mutual solubility curve, the composition of the vapours becomes identical with one of the liquid phases. In the course of the condensation, only one liquid phase increases in quantity. If the point representing the composition of vapours which coexist with two liquid phases is found outside the turbidity line, the quantities of liquid phases in the course of evaporation or condensation vary inversely. For instance, the evaporation of the heteroazeotrope $t_A Q' P' t_{H_{k+1}}$ (Fig. 2) should lead to an increase in the amount of the phase P' associated with a simultaneous decrease in the amount of the phase Q' .

The phenomena described above demonstrate in the properties of the boiling temperature isobars observed the gradual change due to the increase of the boiling temperature of the homologue H_i , belonging to the (H) series.

Summary

1. Two schemes are presented, showing the formation of zeotropes and azeotropes, in one-liquid and two-liquid phase systems in the (A, H_i) series of binary mixtures formed by the agent A and the representatives of the homologous series (H) .

2. For simplification, it is assumed that there is one common single turbidity line for the whole series of (A, H_i) systems.

3. The phenomena occurring depend upon the relative position of the boiling temperature of the agent A , and the critical solubility temperature t_c .

4. As regards heteroazeotropes, discussion is entered into concerning the phenomena occurring in the course of isothermal condensation or evaporation, when the composition of vapour, coexisting with two liquid phases, is found outside the turbidity line.

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Heteroazeotropic Binary Systems. III. Series of (A, H_i) Systems Formed by Regular Solutions

by

J. STECKI

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1. Introductory remarks. In the previous paper [1] the boiling temperature isobars of a series (A, H_i) were described in the case of the partial mutual miscibility of the components in the liquid state, and an ideal scheme of such a system was discussed. Writing the symbol (A, H_i) we signified a series of binary mixtures, formed by a component, termed agent A , with several homologues [2], [11], [12]. The purpose of this paper is to discuss the ideal scheme [1] presented above in the case of these systems being considered as regular mixtures [6], [10]. Therefore, the activity coefficients f_A and f_{H_i} of the components A and H_i , at temperature T , are assumed to depend upon the mole fractions of the components x_A and x_{H_i} in the following way:

$$(1a) \quad RT \log f_A = w_{A,H_i} x_{H_i}^2,$$

$$(1b) \quad RT \log f_{H_i} = w_{A,H_i} x_A^2,$$

where R is the gas constant, and w that which characterises the particular binary mixture A, H_i . It is further assumed that these values are equal to one another for the whole series,

$$(2) \quad w_{A,H_1} = w_{A,H_2} = \dots = w.$$

Both these assumptions have already been made by Prigogine [6], and by Malesiński [3]–[5], in their examination of certain series of binary positive homoazeotropes. For the sake of simplicity, we assume also that the w -values are independent of temperature. In some equations, the latter assumption does not play any important role.

The assumption expressed by Equation (2) arises from the ideal scheme previously described [1]. If w fulfils condition (2), then all the

turbidity lines cover one another, so that they are represented by a single common curve. We recall also that $w = 2RT_c - T_c$ being the critical solubility temperature. Equation (2) is then a rough approximation. Frequently, a smooth curve—critical temperature versus critical composition—may be obtained; these interesting regularities may be examined on the basis of statistical theories of non-athermal r -mer mixtures. In some cases, however, the w -values are almost constant within the given series (A, H_i).

2. Liquid-vapour equilibrium at constant pressure. Let us consider first the isobaric liquid-vapour equilibrium of a single system composed of A and H_i . This equilibrium is represented both by the boiling isobar and by the dew point curve. If a partial miscibility of the components takes place, the equilibrium diagram represents one of the three possible cases: the *heteroazeotrope* (2), the *heterozeotrope* (2), or the so-called (8) *homoazeotrope outside the miscibility gap*. The last named case cannot be identified with the heterozeotrope, since the homoazeotropic point is found on the isobar. Several characteristic points may be distinguished; the boiling temperatures of the components, which we denote by T_A and T_{H_i} ; the homoazeotropic point Az ; and finally three points associated with equilibrium of the three phases. They represent the two liquid phases and one vapour phase. If we examine the whole series, the T_{H_i} value undergoes changes and T_A remains constant; therefore, instead of the three points the corresponding three curves appear. The examination of these curves is one of the purposes of the present paper, which also sets out to examine the limits of the existence of the particular types of isobaric equilibria. These limits are represented by corresponding sections on the T_H axis [1].

In so far as it concerns the single isobars, or, rather, its characteristic four points, we may say, first, that the position of the homoazeotropic point is expressed by the relation between the boiling temperature of the azeotrope, T_{Az} , and its composition, x_{Az} [3], [4]:

$$(3) \quad T_A - T_{Az} = 0.5 Z x_{H_i}^2,$$

which, according to Malesiński [3], [4], [6], are related to the boiling temperature of the respective homologue H_i :

$$(4) \quad x_{H_i} = 1/2 + \frac{T_A - T_{H_i}}{Z},$$

in which Z is the azeotropic range of A in relation to the series (H), [11], [12]; this is equal to

$$(5) \quad Z_A(H) \equiv Z = 2w/\Delta S = 4RT_c/\Delta S,$$

ΔS being the entropy of evaporation. At temperature T , the compositions of the liquid phases of the three-phase system are determined by the Eq. of the turbidity line [6], [10]:

$$(6) \quad 2T_c/T = (2x^* - 1)/\log \frac{x^*}{1 - x^*},$$

in which x^* is the solubility of A in H_i equal to that of H_i in A . The vapour composition [9], expressed in mole fractions of H_i depends only on vapour pressures of pure components:

$$(7) \quad y_{H_i} = \frac{p_{H_i}^0}{p_{H_i}^0 + p_A^0}.$$

It was previously shown [9] that the total vapour pressure of the saturated solutions is:

$$(8) \quad P = (p_{H_i}^0 + p_A^0)x^* e^{(W/RT)(1-x^*)} = (p_{H_i}^0 + p_A^0)a(x^*, T).$$

Here $a(x^*, T)$ stands for the activity of any component at its saturation concentration.

In order to consider the isobaric equilibrium, the last equations should be transformed by means of appropriate expressions for the vapour pressures of the components. We assume that

$$(9) \quad p_A^0/P = \exp \left\{ \frac{\Delta S}{R} (1 - T_A/T) \right\} \quad \text{and} \quad p_{H_i}^0/P = \exp \left\{ \frac{\Delta S}{R} (1 - T_{H_i}/T) \right\},$$

and we consider all entropies of evaporation as equal to one another. Substituting the Eq. (9), by the Eq. (7) and the Eq. (8), we obtain:

$$(10) \quad \log y/(1-y) = \frac{\Delta S}{RT} (T_A - T_{H_i}),$$

$$(11) \quad 1 = \left\{ \exp \left[\frac{\Delta S}{R} (1 - T_A/T) \right] + \exp \left[\frac{\Delta S}{R} (1 - T_{H_i}/T) \right] \right\} a(x^*, T),$$

$$(12) \quad 1 - y = \exp \left[\frac{\Delta S}{R} (1 - T_A/T) \right] a(x^*, T).$$

This is sufficient for the examination of the characteristic lines associated with the isobaric equilibria of the series (A, H) , as mentioned above. The points at the ends of each of the horizontal sections of the boiling isobars lie on the turbidity line (Eq. (7)). The vapour phase compositions, y , as the function of the boiling temperature, T , trace an exponential line (Eq. (12)). The boiling temperature, T , is related to T_{H_i} by means of Eq. (11). Finally, the parabolic curve characteristic for homoazeotropes is described by the Eq. (3).

3. Series (A, H). Consider first the case, in which the boiling temperature of the agent, T_A , is sufficiently low to prevent the appearance of homozeotropic isobars, formed with high boiling homologues. This is discussed later in detail. Fig. 1, which illustrates such a case, is similar

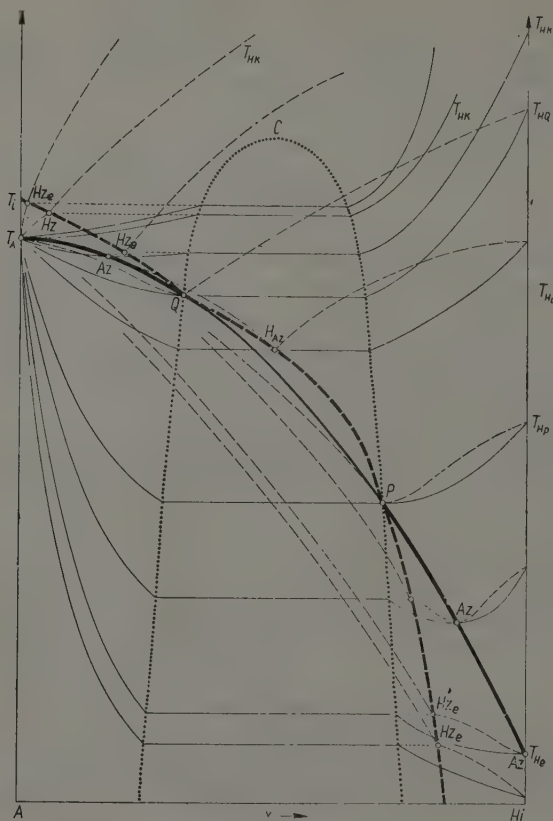


Fig. 1. Boiling temperature isobars and dew point curves of series of binary systems (A, H_i) in the case of relatively low boiling agent A.

to that previously given (Fig. 2 of [1]). The thin lines in Fig. 1 represent the boiling temperature isobars a, b, c, d, \dots , the broken lines represent the dew point curves a', b', c', d', \dots , the thick lines are the characteristic curves, mentioned in the previous paragraph. Then we find the dotted turbidity line MCN , the homoazeotropic parabola, and the broken thick line, on which lie the points representing the vapour in equilibrium with two liquid phases. On section QP , inside the turbidity curve,

the respective points are called heteroazeotropic; on the other hand, points outside the turbidity line should be called heterozeotropic. At points P and Q occurs the transition (2) of heteroazeotropes into homoazeotropes, if the respective homologue really exists.

The boiling temperatures T_{H_P} , T_{H_Q} may be calculated from the implicit relations resulting from the fact that at P or Q all the three lines mentioned above intersect one another, as is shown in Fig. 1. The difference

$$(13) \quad Z_{HeAz} = T_{H_Q} - T_{H_P}$$

characterises the boiling temperature range of the boiling temperature of those homologues which form heteroazeotropes. Outside this range homoazeotropes may exist only within the limits T_{H_e} and T_{H_k} [1], [11], [12]. The homologues H_e and H_k form tangent azeotropes [11], [12] with A . In our case of symmetrical azeotropic ranges, according to Świątosławski's definition, somewhat modified in the previous paper [1], we have

$$(14) \quad T_{H_k} = T_A + 0.5Z,$$

$$(15) \quad T_{H_e} = T_A - 0.5Z,$$

where $Z = Z_A(H)$ is the azeotropic range. It is to be noted that $Z_{HeAz} < Z$, since in all cases $T_{H_Q} < T_{H_k}$ and $T_{H_P} > T_{H_e}$. The limiting conditions of the relation (12) are:

$$(16) \quad \text{if } y \rightarrow 1 (y_A \rightarrow 0), \quad \text{then } T_{H_i} \rightarrow 0, \quad \text{and } T \rightarrow 0;$$

and

$$(17) \quad \text{if } y \rightarrow 0 (y_A \rightarrow 1), \quad \text{then } T_{H_i} \rightarrow \infty, \quad \text{and } T \rightarrow T_l.$$

T_l is given by the relation

$$(18) \quad -\log a(x^*(T), T) = \frac{\Delta S}{R} (1 - T_A/T).$$

This is a result of the Eq. (12), if the Eq. (17) is taken into consideration. Therefore, T_l is the maximum boiling temperature of two-liquid phase systems, in a given series (A , H_i). It is easy to see that, unless this limiting value does not exceed T_c , the formation of homoazeotropes is not possible. If $\Delta S = 20$ e. u., then, approximatively, $T_l = 0.98 T_c$, and the condition mentioned at the beginning of this paragraph is

$$(19) \quad T_A < 0.98 T_c.$$

The value $0.02 T_c$ is of the order of 8°C ., if t_c is relatively high (for instance 130°C .). All these considerations are illustrated in Fig. 1, and summarised below in the list of possible types of equilibrium, together with the corresponding boiling temperature ranges; in the last column is given the symbol of the temperature range

Temp. range	Kind of system	Symbol
$0 \div T_{H_e}$	heteroazeotropes	Z'_{HeZe}
$T_{H_e} \div T_{H_P}$	homoazeotropes besides misc. gap	Z'_{HoAz}
$T_{H_P} \div T_{H_Q}$	heteroazeotropes	Z_{HoAz}
$T_{H_Q} \div T_{H_k}$	homoazeotropes besides misc. gap	Z''_{HoAz}
$T_{H_k} \div \infty$	heteroazeotropes	Z''_{HeZe}

If all possible boiling temperatures of different agents are taken into consideration, the possibility cannot be excluded of the appearance of homozeotropes and also homoazeotropes without any horizontal section on the boiling isobars. If T_A is somewhat higher than $0.98 T_c$, a horizontal section on the tangent boiling isobar remains. In this case the following types of equilibria may be expected:

Temp. range	Kind of system	Symbol
$0 \div T_{H_e}$	heteroazeotropes	Z_{HeZe}
$T_{H_e} \div T_{H_P}$	homoazeotropes besides m. gap	Z'_{HoAz}
$T_{H_P} \div T_{H_Q}$	heteroazeotropes	Z_{HeAz}
$T_{H_Q} \div T_{H_k}$	homoazeotropes besides m. gap	Z'_{HoAz}
$T_{H_k} \div T_t$	heteroazeotropes	Z'_{HeZe}
$T_t \div \infty$	homozeotropes	Z_{HoZe}

T_t stands for the boiling temperature of that homologue forming with A the boiling isobar which crosses exactly the critical miscibility point C . Therefore, we have

$$(20) \quad T_t = T_c - \frac{Z}{4} \log [(0.8244)^{-1} - e^{(4/Z)(T_c - T_A)}],$$

since, at the critical point, $\log a(1/2, T_c) = 0.8244$. These conclusions are valid, unless $T_t < T_{H_k}$. If $T_{H_k} = T_t$, then the tangent boiling isobar intersects exactly the critical miscibility point, so that the Eq. (20) reduces to

$$(21) \quad 1 - T_A/T_c = -\frac{R}{\Delta S} \log [0.8244 (1/e^{-2})] \approx 0.007.$$

Thus, the condition $T_t < T_{H_k}$ implies $T_A < 0.993 T_c$, and the above list of the kinds of system is valid if $0.98 T_c < T_A < 0.993 T_c$. On the contrary, if $T_A > 0.993 T_c$, there must be no horizontal section on the upper tangent boiling temperature isobar $T_A T_{H_k}$. Consequently, we must change the conclusions in the following way:

Temp. range	Kind of system	Symbol
$0 \div T_{H_e}$	heteroazeotropes	Z'_{HeZe}
$T_{H_e} \div T_{H_P}$	homoazeotropes besides misc. gap.	Z'_{HoAz}
$T_{H_P} \div T_{H_Q}$	heteroazeotropes	Z_{HeAz}
$T_{H_Q} \div T_i$	homoazeotropes besides misc. gap.	Z''_{HoAz}
$T_i \div T_{H_k}$	homoazeotropes without horizontal section	Z''_{HoAz}
$T_{H_k} \div \infty$	homozeotropes	Z'_{HoZe}

Such a case should be encountered each time, if T_A is higher than T_c . Fig. 2 represents such a system, in which $T_A = T_c$. The broken thick curve, representing the composition of vapours of three phase systems is drawn for temperatures lower than T_c .

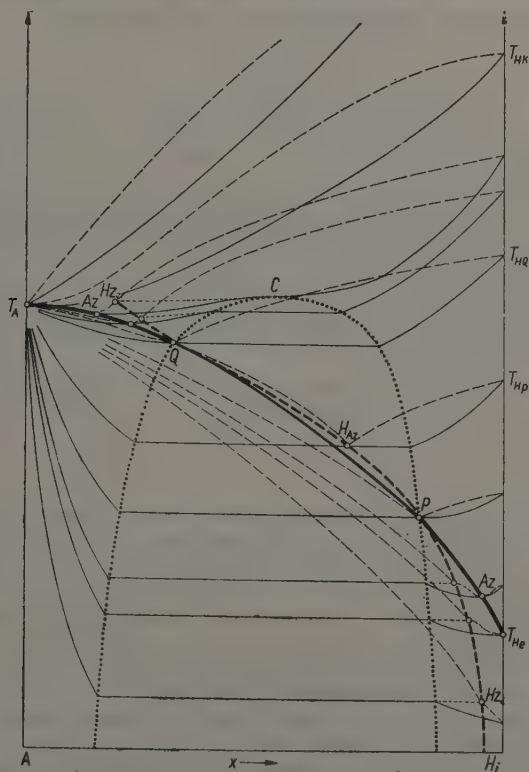


Fig. 2. Scheme representing the boiling temperature isobars and the dew point curves for the systems (A, H_i) . The characteristic lines for the system are shown for the particular case in which $T_A = T_c$.

It should be emphasised that the values limiting the particular boiling temperature ranges of T_A should be regarded as qualitatively true. Those considerations lead, however, to certain conclusions of less restricted importance. It is easy to see that in the cases in which agent A boils lower than T_c , homoazeotropes may be formed without any horizontal section on the boiling temperature isobar, if T_A is slightly lower than T_c . A somewhat larger temperature difference $T_A - T_c$ may be admitted if homoazeotropes are considered. Therefore, it is almost impossible for the boiling temperature isobars to pass over the turbidity line without any horizontal section in those cases in which the lower boiling component boils lower than the critical solubility temperature.

It must be added that in certain recent papers, experiments were described as carried out on the methanol - $n\text{-C}_x\text{H}_{2x+2}$ [13] and acetonitrile-hydrocarbons [14] series. The second example is very similar to the case, shown in Fig. 1. Quantitative comparison was impossible, since the heteroazeotropic compositions were not measured.

Summary

1. The relations derived previously [9] expressing the composition of vapour phase in binary two-liquid vapour systems, are respectively transformed for constant pressure conditions.

2. The behaviour of a series of systems (A, H_i), formed by agent A with the representatives of the series (H) is described on the basis of the previous general considerations [1].

3. The conclusion is drawn that the appearance of homoazeotropes or homoazeotropes without horizontal section of the boiling temperature isobar is almost impossible if the boiling temperature of the lower boiling component is lower than the critical miscibility temperature.

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Equilibrium Constant of Reversible Chemical Reactions

by

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Presented on October 26, 1956

The law of chemical equilibrium, first defined by Guldberg and Waage, has proved of considerable significance in chemistry and other related fields. However, it must be stressed that the formula for the equilibrium constant deduced by these scientists corresponded to the ideal and not to the real state of the gases taking part in the reaction. An attempt to modify the law of equilibrium in accordance with the real state of gases was made by Brodski [1], who substituted the pressure of the gaseous constituents in the equilibrium constant by their fugacity. Such an approach has undoubtedly advanced the solution of the problem, but it is our opinion that the formula for the equilibrium constant as modified by Brodski does not fully correspond to the actual conditions and is deficient especially when solids under high pressures take part in reactions.

The aim of the present considerations is to define the law of equilibrium in a manner allowing it to be used for calculating the equilibrium constant with due regard to the true conditions in which chemical reactions take place.

1. General formula for the equilibrium constant

1.1. The substances taking part in the reaction undergo no change of state in the range from the standard temperature T° to temperature T .

Let us consider a system of substances in a state of equilibrium at temperature T and pressure P . The reaction taking place between the constituents of the system may be symbolically presented in the form



where $\sum A$ are the substrates and $\sum B$ the products of reaction.

It follows from the conditions of equilibrium that

$$(2) \quad \Delta \mu_i k_i = 0,$$

where μ is the chemical potential, and k represents the stoichiometric coefficients.

Equation (2) may also be written in the form

$$(3) \quad \sum_{i=1}^n (\mu_i k_i)_B = \sum_{i=1}^n (\mu_i k_i)_A.$$

In accordance with an earlier work [2]

$$(4) \quad \mu = -\varphi_T^0 + RT \ln \Phi + H^0 - TS^0,$$

where

$$\begin{aligned} \varphi_T^0 = & a \left(T^0 - T + T \ln \frac{T}{T^0} \right) + \frac{b}{2} (T - T^0)^2 + \\ & + \frac{c}{2} \frac{(T - T^0)^2}{T^{20} T} + \frac{d}{6} [T^3 - T^{20} (2T^0 - 3T)], \end{aligned}$$

and the coefficients a , b , c and d are computed from the formula for the specific molar heat:

$$C_p = a + bT + cT^{-2} + dT^2,$$

Φ = substitute pressure, defined from the formula

$$RT \ln \Phi = \int_{1 \text{ atm}}^P V dP,$$

and H^0 and S^0 denote standard enthalpy and standard entropy of the substance, respectively.

From equations (3) and (4) we obtain

$$\begin{aligned} (5) \quad \sum_{i=1}^n (-\varphi_T^0 + RT \ln \Phi + H^0 - TS^0)_{iB} \cdot k_{iB} = \\ = \sum_{i=1}^n (-\varphi_T^0 + RT \ln \Phi + H^0 - TS^0)_{iA} \cdot k_{iA}. \end{aligned}$$

Relation (5) may be written in the following form:

$$\begin{aligned} (6) \quad -RT \sum_{i=1}^n k_{iB} \ln \Phi_{iB} + RT \sum_{i=1}^n k_{iA} \ln \Phi_{iA} = \\ = \sum_{i=1}^n (-\varphi_T^0 + H^0 - TS^0)_{iB} k_{iB} - \sum_{i=1}^n (-\varphi_T^0 + H^0 - TS^0)_{iA} k_{iA} \end{aligned}$$

or

$$(7) \quad -RT \sum_{i=1}^n k_{iB} \ln \Phi_{iB} + RT \sum_{i=1}^n k_{iA} \ln \Phi_{iA} = \Delta H^0 - \Delta \varphi_T^0 - T \Delta S^0,$$

where ΔH^0 represents the change of enthalpy of the reaction in standard conditions, Δq_T^0 — the value which can be calculated from specific molar heats of the constituents and ΔS^0 — the algebraic sum of standard entropies calculated from the equation

$$\Delta S^0 = \sum S_B^0 - \sum S_A^0.$$

All the values appearing on the right-hand side of equation (7) refer to the pressure of 1 atmosphere and express the changes of the standard free energy of the system which are usually denoted by ΔF_T^0 :

$$(8) \quad \Delta F_T^0 = \Delta H^0 - \Delta q_T^0 - T \Delta S^0.$$

From equations (7) and (8) we obtain

$$(9) \quad \Delta F_T^0 = -RT \sum_{i=1}^n k_{iB} \ln \phi_{iB} + RT \sum_{i=1}^n k_{iA} \ln \phi_{iA},$$

and by introducing the symbol K_ϕ to denote the equilibrium constant of reversible chemical reactions with due regard to substitute pressure, we obtain

$$(10) \quad \Delta F_T^0 = -RT \ln K_\phi$$

and

$$(11) \quad K_\phi = \frac{[\phi_1^{k_1} \cdot \phi_2^{k_2} \cdot \dots]_B}{[\phi_1^{k_1} \cdot \phi_2^{k_2} \cdot \dots]_A}.$$

1.2. The substances taking part in the reversible reaction undergo changes of state within the temperature range from T^0 to T .

The formulae deduced for the equilibrium constant can be applied also in the case when the substances taking part in the reaction display a change of state in the temperature range from T^0 (standard) to T . In this case the change of standard free energy must be calculated taking into account the variation of state of the constituents in the system, for instance, in the change from state α to state ω ; we obtain:

$$(12) \quad \Delta F_T^0 = \Delta H_\alpha^0 \mp \Delta H_{\alpha \rightarrow \omega}^0 - \Delta q_{T_\omega}^0 - T(\Delta S_\alpha^0 \mp \Delta S_{\alpha \rightarrow \omega}^0).$$

2. Discussion of the formula

The concept of substitute pressure refers to all substances, both gaseous and condensed; the formula deduced here is thus of a general nature, and serves to define the equilibrium constant of a system in which a chemical reaction takes place.

If gases only take part in the reaction, then for real gases the following formula considering the substitute pressure must be used:

$$(13) \quad K_{\phi} = \frac{[\bar{\phi}_1^{k_1} \cdot \bar{\phi}_2^{k_2} \cdot \dots]_{B \text{ gases}}}{[\bar{\phi}_1^{k_1} \cdot \bar{\phi}_2^{k_2} \cdot \dots]_{A \text{ gases}}},$$

where $\bar{\phi}_1, \bar{\phi}_2$, etc. represent the substitute pressures of the gaseous constituents.

On the other hand, in the case of perfect gases, or when it is assumed that the gases taking part in the reaction behave like a perfect gas, the formula for the equilibrium constant deduced by Guldberg and Waage is obtained as a special case of relation (13):

$$(14) \quad K_p = \frac{[\bar{P}_1^{k_1} \cdot \bar{P}_2^{k_2} \cdot \dots]_{B \text{ gases}}}{[\bar{P}_1^{k_1} \cdot \bar{P}_2^{k_2} \cdot \dots]_{A \text{ gases}}},$$

where \bar{P}_1, \bar{P}_2 , etc. represent the pressures of the corresponding gaseous constituents.

When a chemical reaction includes, besides gases, also condensed substances, then two possibilities must be considered:

- a) the condensed substances do not form solutions;
- b) the condensed substances form solutions.

In the first case the equilibrium constant is expressed by the following formula:

$$(15) \quad K_{\phi} = \frac{[\bar{\phi}_1^{k_1} \cdot \bar{\phi}_2^{k_2} \cdot \dots]_{B \text{ gases}} \cdot [\bar{\phi}_1^{k_1} \cdot \bar{\phi}_2^{k_2} \cdot \dots]_{B \text{ condensed}}}{[\bar{\phi}_1^{k_1} \cdot \bar{\phi}_2^{k_2} \cdot \dots]_{A \text{ gases}} \cdot [\bar{\phi}_1^{k_1} \cdot \bar{\phi}_2^{k_2} \cdot \dots]_{A \text{ condensed}}}.$$

In the latter case the formula must account for substitute pressures $\bar{\phi}$ of condensed constituents in solution:

$$(16) \quad K_{\phi} = \frac{[\bar{\phi}_1^{k_1} \cdot \bar{\phi}_2^{k_2} \cdot \dots]_{B \text{ gases}} \cdot [\bar{\phi}_1^{k_1} \cdot \bar{\phi}_2^{k_2} \cdot \dots]_{B \text{ condensed}}}{[\bar{\phi}_1^{k_1} \cdot \bar{\phi}_2^{k_2} \cdot \dots]_{A \text{ gases}} \cdot [\bar{\phi}_1^{k_1} \cdot \bar{\phi}_2^{k_2} \cdot \dots]_{A \text{ condensed}}}.$$

The substitute pressure of constituents may be represented as the product of the activity of a constituent in the condensed solution and of the substitute pressure of the constituent in the pure state:

$$(17) \quad \bar{\phi}_i = a_i \cdot \phi_i.$$

By introducing the relation (17) into formula (16) we obtain after transformation:

$$(18) \quad k_{\phi} = \frac{[\bar{\phi}_1^{k_1} \cdot \bar{\phi}_2^{k_2} \cdot \dots]_{B \text{ gases}} \cdot [a_1^{k_1} \cdot a_2^{k_2} \cdot \dots]_{B \text{ condensed}} \cdot [\phi_1^{k_1} \cdot \phi_2^{k_2} \cdot \dots]_{B \text{ condensed}}}{[\bar{\phi}_1^{k_1} \cdot \bar{\phi}_2^{k_2} \cdot \dots]_{A \text{ gases}} \cdot [a_1^{k_1} \cdot a_2^{k_2} \cdot \dots]_{A \text{ condensed}} \cdot [\phi_1^{k_1} \cdot \phi_2^{k_2} \cdot \dots]_{A \text{ condensed}}}.$$

The substitute pressures of condensed substance differ only slightly for a wide range of pressures and because of this they can be replaced by one value only: $\Phi_1 \simeq \Phi_2 \simeq \Phi_3 \simeq \dots \simeq \Phi_u$. When this assumption is made, Φ_u may be regarded at the same time as the substitute pressure of the condensed system.

$$(19) \quad \frac{[\Phi_1^{k_1} \cdot \Phi_2^{k_2} \cdot \dots]_{B \text{ condensed}}}{[\Phi_1^{k_1} \cdot \Phi_2^{k_2} \cdot \dots]_{A \text{ condensed}}} \simeq \Phi_u^{\Delta k_i},$$

where

$$\Delta k_i = \sum_{i=1}^n k_{i \text{ B condensed}} - \sum_{i=1}^n k_{i \text{ A condensed}}.$$

From (18) and (19) we have

$$(20) \quad K_\Phi = \frac{[\bar{\Phi}_1^{k_1} \cdot \bar{\Phi}_2^{k_2} \cdot \dots]_{B \text{ gases}} \cdot [\bar{a}_1^{k_1} \cdot \bar{a}_2^{k_2} \cdot \dots]_{B \text{ condensed}}}{[\bar{\Phi}_1^{k_1} \cdot \bar{\Phi}_2^{k_2} \cdot \dots]_{A \text{ gases}} \cdot [\bar{a}_1^{k_1} \cdot \bar{a}_2^{k_2} \cdot \dots]_{A \text{ condensed}}} \cdot \Phi_u^{\Delta k_i}.$$

When the pressure is not too high, and $\Phi_u = 1$, then formula (20) can be simplified:

$$(21) \quad K_\Phi = \frac{[\bar{\Phi}_1^{k_1} \cdot \bar{\Phi}_2^{k_2} \cdot \dots]_{B \text{ gases}} \cdot [\bar{a}_1^{k_1} \cdot \bar{a}_2^{k_2} \cdot \dots]_{B \text{ condensed}}}{[\bar{\Phi}_1^{k_1} \cdot \bar{\Phi}_2^{k_2} \cdot \dots]_{A \text{ gases}} \cdot [\bar{a}_1^{k_1} \cdot \bar{a}_2^{k_2} \cdot \dots]_{A \text{ condensed}}}.$$

If the pressure is small (about 1 atmosphere) and condensed substances only take part in the reversible reaction, then the simplified formula will assume the following form:

$$(22) \quad K_a = \frac{[\bar{a}_1^{k_1} \cdot \bar{a}_2^{k_2} \cdot \dots]_{B \text{ condensed}}}{[\bar{a}_1^{k_1} \cdot \bar{a}_2^{k_2} \cdot \dots]_{A \text{ condensed}}}.$$

In this particular case, in accordance with the generally accepted principles, the equilibrium constant is denoted by K_a .

3. Conclusions

It follows from the foregoing discussion that the formula deduced in the first part of this paper has a general character and that other formulae for the equilibrium constant, K_p and K_a , used hitherto, are only its special forms resulting from it after some conventional, simplifying assumptions have been made. However, it is to be stressed that all such simplifications always give a distorted definition of the chemical reaction. Moreover, when reactions develop under high pressures the formulae commonly used hitherto fail entirely. On the other hand,

the formula here deduced makes it possible to compute the equilibrium constant when the true properties of substances taking part in a reversible chemical reaction are taken under consideration.

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On the Relation between the Composition of Binary and Ternary Azeotropes

by

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Presented by W. ŚWIEȚOSŁAWSKI on October 29, 1956

1. Introductory remarks. In the present considerations concerning ternary positive, positive-negative (saddle) and negative azeotropy a discussion is entered into as regards the relation between the composition of the ternary and of the binary azeotropes formed by three components [1], [2]. The possibility of the formation of ternary azeotropes is also considered in the case wherein one or even two of the binary systems are zeotropic.

2. Composition of the ternary homoazeotrope, parameters a , b and c , auxiliary lines, and their common crossing point. The general relation between the compositions of the binary and the ternary azeotropes was expressed in the following way [1]:

$$(1) \quad x_i^{(ij)} - x_i + x_k \frac{z_{ik} - z_{ij} - z_{jk}}{2z_{ij}} = 0,$$

$x_i^{(ij)}$ being the mole fraction of i in the binary azeotrope $Az(ij)$, x_i and x_k — those of the components i and k in the ternary azeotrope, and z — the half-value of the symmetrical azeotropic range in the respective binary systems.

If the equation (1) is taken into consideration for the system of components 1, 2 and 3, the compositions of the respective binary azeotropes are combined with that of the ternary azeotrope by the equations:

$$(2a) \quad x_1^{(12)} - x_1 + ax_3 = 0,$$

$$(2b) \quad x_3^{(23)} - x_3 + bx_1 = 0,$$

$$(2c) \quad x_1^{(13)} - x_1 + cx_2 = 0,$$

in which the constants a , b and c are:

$$(3a) \quad a = \frac{z_{13} - z_{12} - z_{23}}{2z_{12}},$$

$$(3b) \quad b = \frac{z_{13} - z_{12} - z_{23}}{2z_{23}},$$

$$(3c) \quad c = \frac{z_{12} - z_{13} - z_{23}}{2z_{13}},$$

and are therefore combined with one another as follows:

$$(4) \quad 2abc + ab + bc + ac + a = 0.$$

The relations (2) are graphically represented in Fig. 1. The straight lines joining the ternary azeotropic point $Az(123)$ with the binary $Az(12)$; $Az(23)$ and $Az(13)$, correspond to the respective equations (2a), (2b) and (2c). The lines cross one another at one point $Az(123)$, because the conditions imposed by the common solution of the equations (2a), (2b) and (2c) are equivalent to the condition previously derived:

$$(5) \quad 2z_{12}x_2^{(12)} + 2z_{23}x_3^{(23)} - 2z_{13}x_3^{(13)} + (z_{13} - z_{23} - z_{12}) = 0.$$

On the other hand, the lines meet the points $Az(12)$, $Az(23)$ and $Az(13)$ because, in accordance with (2), if $x_3 = 0$, $x_1 = x_1^{(12)}$, if $x_1 = 0$, $x_3 = x_3^{(23)}$, and if $x_2 = 0$, $x_1 = x_1^{(13)}$.

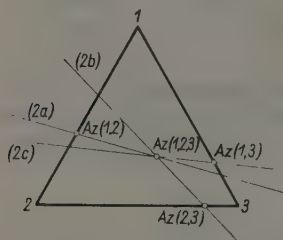


Fig. 1. Straight lines (2a), (2b) and (2c) in the system of coordinates determined by the concentration triangle

Below is described the graphic method of determining the composition of ternary azeotropes. It is consistent with the analytical method [1]. This method consists in drawing the lines (2a), (2b) and (2c) with the aid of known values of the parameters a , b and c and of the binary azeotropic compositions. The knowledge of two parameters only and compositions of two binary azeotropes suffices for this purpose. The remainder may be calculated from (4) and (5). The geometrical construction may be easily built up by means of three auxiliary

lines which correspond to a particular case of lines (2a), (2b) and (2c). They pass through points:

$$(2a): x_3 = 1, x_1, x_2 = 0; \quad (2b): x_1 = 1, x_2, x_3 = 0; \quad (2c): x_2 = 1, x_1, x_3 = 0,$$

and are expressed by the equations

$$(6a) \quad x_1 - a(x_3 - 1) = 0,$$

$$(6b) \quad x_3 - b(x_1 - 1) = 0,$$

$$(6c) \quad x_1 - c(x_2 - 1) = 0.$$

The lines pass through the corners of the triangle, and, according to (6), the sides of the triangle at points $x_1^{(12)} = -a$, $x_3^{(23)} = -b$, $x_1^{(13)} = -c$. By way of explanation, an example is given in Fig. 2. The lines cross one another at the common point W . This is consequent on the identity of (5) with the condition of the common solution of the equations (6). The two auxiliary lines determine the third line and the third parameter. Lines (2a), (2b) and (2c) are then drawn through points $Az(12)$, $Az(23)$ and $Az(13)$ parallel to the respective auxiliary lines. This is shown in Fig. 3.

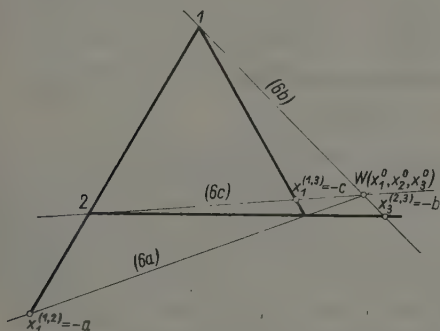


Fig. 2. The auxiliary lines in the case of $a > 0$, $b < -1$ and c lying in the interval $(0, -1)$.

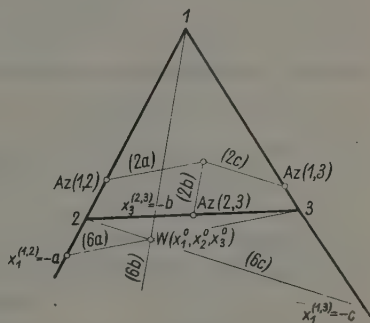


Fig. 3. Graphic method of determining the composition of ternary azeotropes $Az\ 123$. The case wherein $a > 0$, $c > 0$, and b in the interval $(0, -1)$

The diagram also shows the correlation between the composition of the binary azeotropes. The co-ordinates of the characteristic point $W(x_1^0, x_2^0, x_3^0)$ may be calculated by solving the system of equations (6a) and (6b):

$$(7) \quad x_1^0 = \frac{a(b+1)}{ab-1}, \quad x_3^0 = \frac{b(a+1)}{ab-1}.$$

The value of x_2^0 emerges then as the difference $x_2^0 = 1 - x_1^0 - x_3^0$. The constants a and b are equal to

$$(8) \quad a = \frac{x_1^0}{x_3^0 - 1}, \quad b = \frac{x_3^0}{x_1^0 - 1}.$$

The c -value then results from (4).

Point W may lie outside or inside the triangle. The possible location of point W depends on the types of ternary azeotropes. This question is discussed below.

3. The position of the auxiliary lines. The position of the auxiliary lines, characterising the individual ternary azeotrope, depends on the values a , b and c , and, of course, upon the W -point co-ordinates. Dif-

ferent types of ternary azeotropes depend directly on the signs of the azeotropic ranges. If all three azeotropic ranges are positive, only positive azeotropes can be formed. In the case of negative ranges, only negative azeotropes appear. If, however, one of the ranges is negative, a positive-negative (saddle) azeotrope is or may be formed. The latter will herein after be called 1-negative azeotrope. If two ranges are negative, the positive-negative azeotrope which may appear is hereinafter called 2-negative azeotrope.

According to the relation (3) we have

$$(9) \quad z_{23}(z_{12}=a)b, \quad z_{13}(z_{12}=2a+a)b+1, \quad z_{13}(z_{23}=2b+b)a+1.$$

Using the equation (8), and bearing in mind that $x_1^0 + x_2^0 + x_3^0 = 1$, we may rearrange relations (9) in the following way:

$$(10) \quad \frac{z_{23}}{z_{12}} = \frac{x_1^0(x_1^0 - 1)}{x_3^0(x_3^0 - 1)}, \quad \frac{z_{13}}{z_{12}} = \frac{x_2^0(x_2^0 - 1)}{x_3^0(x_3^0 - 1)}, \quad \frac{z_{13}}{z_{23}} = \frac{x_2^0(x_2^0 - 1)}{x_1^0(x_1^0 - 1)}.$$

If the system is a positive or a negative azeotrope, all quotients of z are positive. Therefore, according to (10), the values x_1^0 , x_2^0 and x_3^0 should lie either all outside or all inside the interval $\langle 0, 1 \rangle$. This condition is presented in Fig. 4. The broken line regions correspond to all possible positions of point W for both the ternary positive or the ternary negative azeotropes. The position of point W in this region gives no conclusive answer as to whether the azeotrope is positive or negative, since the parameters and the auxiliary lines may be identical in both cases. The decisive factors are the signs of the azeotropic ranges.

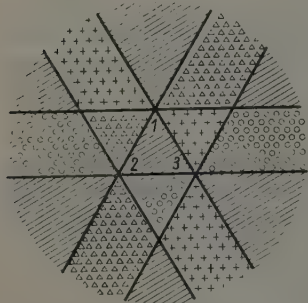


Fig. 4. Regions of possible locations of point W . Broken lines — positive or negative ternary azeotropes. Crosses — 2-negative ternary azeotropes (only $z_1 > 0$). Circles — 1-negative ternary azeotropes (only $z_{23} < 0$). Triangle — 1-negative ternary azeotropes (only $z_{13} < 0$).

It will be shown below that the remaining regions in Fig. 4 correspond to positive-negative azeotropic systems.

In order to give a subdivision of the regions in which point W may lie in the two types of ternary positive-negative azeotropes, we have to assume that in system (13) there is always formed a positive azeotrope, or at least azeotrope showing positive deviations from Raoult's law.

In the case of a 2-negative ternary azeotrope, values z_{13}/z_{12} and z_{13}/z_{23} are negative, and z_{23}/z_{12} is positive. Then x_1^0 and x_3^0 lie within $\langle 0, 1 \rangle$, and x_2^0 — outside this interval; or, on the other hand, x_2^0 — lies inside,

and x_1^0 and x_3^0 — outside this interval. In Fig. 4, the field of 2-negative azeotropy is denoted by crosses.

In the region of 1-negative azeotropes two cases may be distinguished: either z_{23} or z_{12} is negative.

(a) If $z_{23} < 0$, then $z_{13}/z_{12} > 0$, $z_{23}/z_{12} < 0$, and $z_{13}/z_{23} < 0$. Consequently, according to (10), the x_2^0 and x_3^0 -values lie within the interval $(0,1)$, and x_1^0 — outside it, or x_1^0 lies inside this interval and then $x_2^0 < 0$, $x_3^0 > 1$, or $x_2^0 > 1$, $x_3^0 < 0$.

(b) If $z_{12} < 0$, then $z_{13}/z_{12} < 0$, $z_{23}/z_{12} < 0$, and $z_{13}/z_{23} > 0$. For this reason x_1^0 and x_2^0 lie within, and x_3^0 outside the interval $0,1$; or x_3^0 — inside it, and then $x_1^0 > 1$, $x_2^0 < 0$, or $x_1^0 < 0$ and $x_2^0 > 1$.

In Figure 4 the circles correspond to the case (a), and the triangles to the case (b).

4. Possibilities of the formation of ternary azeotropes when one or two binary systems are zeotropic. The formation of a ternary azeotrope is not necessarily associated with the existence of three binary azeotropes. Fig. 5 represents different possibilities in the formation of ternary azeotropes if one or even two of the binary systems form zeotropic mixtures.

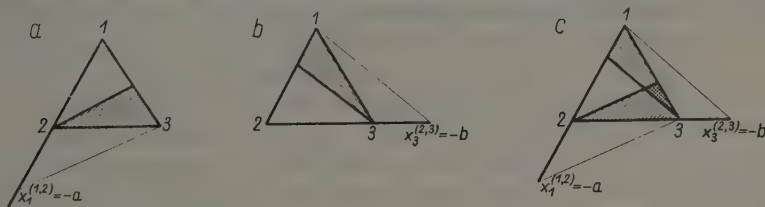


Fig. 5. Broken line regions corresponding to possible compositions of ternary azeotropes $Az(123)$ when:

- (a) system (12) is zeotropic, and $a > 0$;
- (b) system (23) is zeotropic, and $b < -1$;
- (c) both systems (12) and (23) are zeotropic, $a > 0$, $b < -1$ (checkered area)

If one of the parameters lies within $(0, -1)$ and if the respective azeotropes $Az(12)$, $Az(23)$ or $Az(13)$ does not exist, the formation of a ternary azeotrope becomes impossible. Such a case is represented in Fig. 5b ($b = -1$, system (23) is zeotropic). If the two azeotropes, $Az(12)$ and $Az(23)$, are non existent, the ternary azeotrope may appear in the common part of both fields (Fig. 5c). This is a particularly rare case. Generally speaking, if two binary systems are zeotropic, and if two coordinates of point W are negative, the appearance of a ternary azeotrope becomes impossible.

Summary

1. Further analysis was made of the previously derived equation (1)

$$(1) \quad x_i^{(ij)} - x_i + x_k \frac{z_{ik} - z_{ij} - z_{jk}}{2z_{ij}} = 0,$$

in which the relation was established between the mole fraction $x_i^{(ij)}$ of component i in the azeotrope $Az(ij)$ and the respective concentrations x_i and x_k in the ternary azeotrope $Az(ijk)$, z_{ik} , z_{ij} and z_{jk} being the respective half values of symmetrical azeotropic ranges.

2. A graphic method of determining the ternary azeotropic composition is presented.

3. The conditions necessary to the formation of ternary azeotropes are given for the case in which one or two binary systems formed by three components are zeotropic.

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Compositions of the Series of Ternary Homoazeotropes

by

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Presented by W. ŚWIĘTOSŁAWSKI on October 29, 1956

1. Introductory remarks. The properties of individual ternary azeotropic mixtures were considered on previous occasions [1]–[3]. It was assumed that the activity coefficients of the components of mixtures studied under isobaric conditions, are defined by the formulas valid for regular solutions. The present considerations are extended to series of regular mixtures, forming positive azeotropes, positive-negative (saddle) azeotropes, or ternary negative azeotropes as yet unknown.

Restricting Świętosławski's general classification of azeotropes [4]–[7] to regular azeotropes, the term "series of azeotropes" is to be assigned to a set of azeotropic systems having the same value of the regular solution constant. Usually, a series of azeotropes is obtained by replacing one of the components by its successive higher or lower boiling homologues. The greater the similarity between the physico-chemical properties of the homologues, the more reasonable it becomes to consider the whole set of azeotropes as a single series. Our considerations are extended to complex series of azeotropes, representing such a set as is obtained by replacing by their homologues not one, but two or more components of a given individual system.

Świętosławski [6], [7] considered the course of fractional distillation of multi-component mixtures comprising different azeotropic agents and several series of homologous compounds. The mixture of components forming one series of azeotropes he called a polyazeotropic system. The mixture of components of more than one series of azeotropes (e. g., when the mixture contains the representatives of two or more homologous series) was called a polyazeotropic mixture.

Different possibilities concerning the formation of individual ternary azeotropes in a polyazeotropic system or mixture are now taken into account from the point of view of Świętosławski's classification. It should be remembered, however, that the existence of components capable of

forming azeotropes in the given series does not necessarily lead to their appearance in the course of distillation of such series or of a polyazeotropic mixture.

2. Composition of individual ternary azeotropes. The composition of the ternary azeotrope was determined [1],[3] as the common crossing point of the straight lines expressed as follows:

$$(1a) \quad x_1^{(12)} - x_1 + ax_3 = 0,$$

$$(1b) \quad x_3^{(23)} - x_3 + bx_1 = 0,$$

$$(1c) \quad x_1^{(13)} - x_1 + cx_2 = 0,$$

where $x_1^{(12)}$, $x_3^{(23)}$ and $x_1^{(13)}$ are the mole fractions of components 1, 2 and 3 in the binary azeotropes, and x_1, x_2, x_3 — those in the ternary azeotropic mixture. The constants a , b and c are equal to

$$(2a) \quad a = \frac{z_{13} - z_{12} - z_{23}}{2z_{12}}, \quad (2b) \quad b = \frac{z_{13} - z_{12} - z_{23}}{2z_{23}}, \quad (2c) \quad c = \frac{z_{12} - z_{13} - z_{23}}{2z_{13}},$$

z is the half value of the symmetric azeotropic range of a given binary system. The geometrical construction relating the compositions of binary and ternary azeotropes has already been given [3]. This construction was based on the following relations characterizing the three auxiliary lines,

$$(3a) \quad x_1 - a(x_3 - 1) = 0,$$

$$(3b) \quad x_3 - b(x_1 - 1) = 0,$$

$$(3c) \quad x_1 - c(x_2 - 1) = 0,$$

which are parallel to lines (1a), (1b) and (1c). These cross one another at the common point W , having the co-ordinates x_1^0, x_2^0, x_3^0 .

3. Compositions of the series of ternary azeotropes. We take into consideration the series of azeotropes $(1_i, 2, 3)$, which is one of the three possible — $(1_i, 2, 3)$, $(1, 2_j, 3)$ and $(1, 2, 3_k)$ — which may be formed from the system $(1, 2, 3)$ by replacing components 1, 2 and 3 by its homologues. We assumed above that the binary regular solution constant remains unchanged for systems formed by successive homologues. Therefore, the value of the azeotropic range also remains constant (the differences in vaporisation entropies of the components disregarded — [8]), as well as the parameters a , b and c the co-ordinates of point W — x_1^0, x_2^0, x_3^0 . In addition, the value of $x_3^{(23)}$ is also constant, because the components 2 and 3 remain the same in the series $(1_i, 2, 3)$. Then the position of line (1b) is invariant. On this line lie the points representing the azeotropic composition of the entire series.

An example of the composition changes in the ternary azeotropes is given in Fig. 1. In this case, the composition changes from points

$Az(1,2,3)$ $Az(2,3)$ to $Az(1,2,3)$ $Az(1,3)$. These points correspond to tangent azeotropes, discussed below. Successive azeotropes $Az(1_i,2,3)$ are related to $Az(1_i,2)$ and $Az(1_i,3)$. As previously shown [3], they lie on a set of straight lines (1a) and (1c), parallel to the auxiliary lines (3a) and (3c). The auxiliaries (3a), (3b) and (3c) are marked by broken lines. They cross the triangle sides or the prolongations of such sides at points $x_1^{(12)} = -a$, $x_3^{(23)} = -b$, $x_1^{(13)} = -c$. Point $W(x_1^0, x_2^0, x_3^0)$ is characteristic of the given series. The case presented in Fig. 1 makes it clear that the formation of ternary azeotropes is possible in spite of the absence of

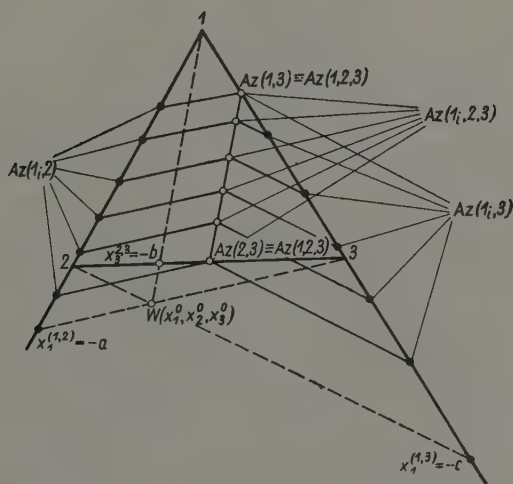


Fig. 1. Series of ternary azeotropes of the type $Az(1_i, 2, 3)$

one or two binary azeotropes in the system, as demonstrated elsewhere [3]. In such a case, an "unreal azeotropic composition" was assigned to zeotropic systems.

4. Complex series of ternary azeotropes. A set of azeotropes formed by a single azeotropic agent with two series of homologues is the simplest case of a complex series of ternary azeotropes.

Consider a complex series of azeotropes $(1_i, 2, 3_k)$ formed by comp. 2 with two series (1_i) and (3_k) . For each successive component 3 of series (3_k) one series of azeotropes $(1_i, 2, 3)$ is obtained. The picture of a complex series $(1_i, 2, 3_k)$ will be repeated for the series $(1_i, 2, 3)$ just as many times as the azeotropes $Az(2, 3_k)$ form ternary azeotropes with at least one of the representatives of the homologous series (1_i) . Fig. 2 represents a possible case of complex series $(1_i, 2, 3_k)$. Four series $(1_i, 2, 3)$ are shown together. The principles of construction are identical with those applying to Fig. 1. It should be emphasized that the characteristic values of a, b, c

and $W(x_1^0, x_2^0, x_3^0)$ remain constant for the given complex series. The azeotropic points $Az(1_i, 3_k)$ and the lines joining them with points $Az(1_i, 2, 3_k)$ (parallel to the auxiliary lines (3c)) were not marked in Fig. 2. Ternary azeotropic points $Az(1_i, 2, 3_k)$, shown by circles, are determined as the cross points of two sets of straight parallel lines — expressed by (1a) and (1b) — drawn through successive points $Az(1_i, 2)$ and $Az(2, 3_k)$. The coincidence of this cross point with the side of the triangle denotes the

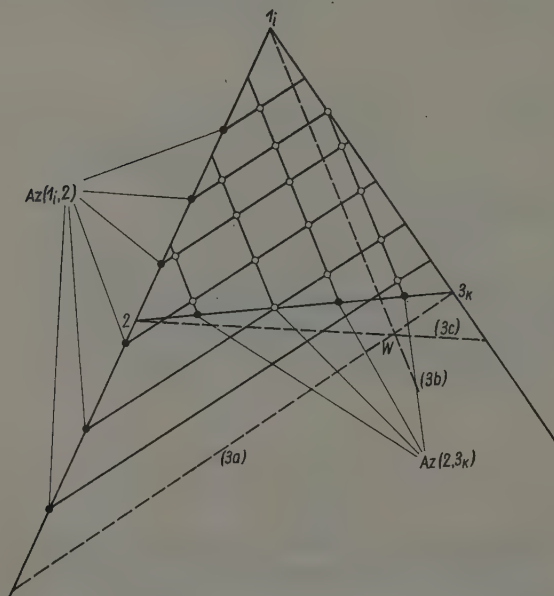


Fig. 2

existence of a tangent ternary azeotrope only when this point corresponds to the binary azeotrope.

In general, the complex series $(1_i, 2, 3_k)$ may be considered as a set of several series of the type $(1, 2, 3_k)$ with successive components of series (1_i) . A more complicated complex series is of the type $(1_i, 2_j, 3_k)$ formed by three homologous series (1_i) , (2_j) and (3_k) . It is clear that the formation of such complex series may be represented as a coexistence of several series $(1_i, 2, 3_k)$ with successive components of series (2_j) .

5. Tangent ternary azeotropes. A tangent azeotrope is one possessing the concentration of one or more components almost equal to zero. In the case of ternary azeotropic mixtures, two types of such azeotropes may exist: (a) ternary azeotrope blending the binary azeotrope, i. e., an azeotrope tangent to the side of the triangle; (b) a ternary azeotrope

blending the corner of the triangle, corresponding to a pure component, i. e., a tangent azeotrope at the corner of the triangle.

(a) Azeotropes tangent to the side of the triangle. Conditions for such an azeotrope are: $x_i = 0$, $x_j + x_k = 1$. The general relation is [1]

$$(4) \quad x_i^{(j)} - x_i + x_k \frac{z_{ik} - z_{ij} - z_{jk}}{2z_{ij}} = 0.$$

Then, for the azeotrope tangent to the side of the triangle, we have

$$(5) \quad x_1^{(ij)} + x_k^{(jk)} \frac{z_{ij} - z_{ij} - z_{jk}}{2z_{ij}} = 0.$$

Applying (5) to the three alternative tangent azeotropes (1,2,3) we obtain the conditions:

$$(6a) \quad \begin{aligned} Az(123) &= Az(23), & x_1 &= 0, & x_2 &= x_2^{(23)}, & x_3 &= x_3^{(23)}, \\ x_1^{(12)} &= -ax_3^{(23)}, & x_1^{(13)} &= -cx_3^{(23)}. \end{aligned}$$

$$(6b) \quad \begin{aligned} Az(123) &= Az(12), & x_3 &= 0, & x_1 &= x_1^{(12)}, & x_2 &= x_2^{(12)}, \\ x_3^{(23)} &= -bx_1^{(12)}, & x_3^{(13)} &= (1+c)x_2^{(12)}. \end{aligned}$$

$$(6c) \quad \begin{aligned} Az(123) &= Az(13), & x_2 &= 0, & x_1 &= x_1^{(13)}, & x_3 &= x_3^{(13)}, \\ x_2^{(12)} &= 1+ax_3^{(13)}, & x_2^{(23)} &= b+1x_1^{(13)}. \end{aligned}$$

In order to form a ternary azeotrope tangent to the side of the triangle, the components should be chosen in such a way that one of the conditions (6) is fulfilled.

The possibility of the appearance of a tangent azeotrope may easily be discussed by way of the analysis of a series of azeotropes. As shown in Fig. 1, such a series does exist between two tangent azeotropes, the upper and the lower. If the series of azeotropes (1₁,2,3) embraces a sufficiently large number of homologues (1₁), it is easy to find an almost tangent azeotrope. In practice, however, such conditions are fulfilled only approximately.

Attention is drawn to the fact that ternary azeotropes formed in the series (1₁,2,3) may lie on different straight lines joining different binary azeotropic points, depending on the value of b and the composition of the azeotrope $Az(23)$. The cases are presented in Figures 4, 5 and 6.

(b) Azeotropes tangent at the corner of the triangle. Conditions for such an azeotrope are $x_1 = 1$, $x_j = 0$, $x_k = 0$. Starting with relation (4), which may be rearranged in different ways, we obtain:

$$(7) \quad x_k^{(jk)} = -\frac{z_{ik} - z_{ij} - z_{jk}}{2z_{jk}}, \quad x_i^{(ij)} = 1, \quad x_i^{(ik)} = 1.$$

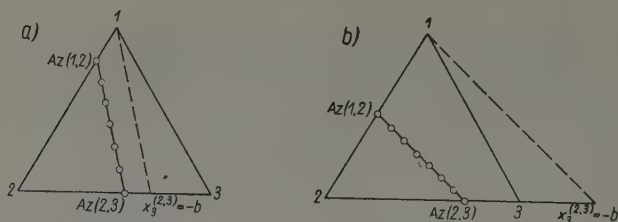


Fig. 3. Series of ternary azeotropes lying between azeotropes $Az(1, 2)$ and $Az(2, 3)$

$$(a) \quad 0 < x_3^{(23)} < -b, \quad 0 > b > -1,$$

$$(b) \quad 0 < x_3^{(23)} < 1, \quad b < -1.$$

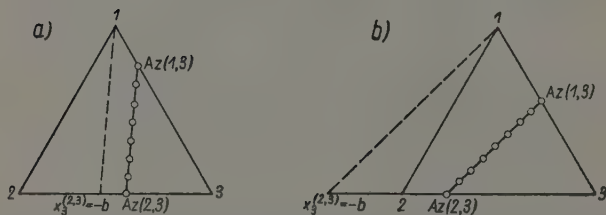


Fig. 4. Series of ternary azeotropes lying between azeotropes $Az(23)$ and $Az(1, 3)$

$$(a) \quad -b < x_3^{(23)} < 1, \quad 0 > b > -1,$$

$$(b) \quad 0 < x_3^{(23)} < -1, \quad b > 0.$$

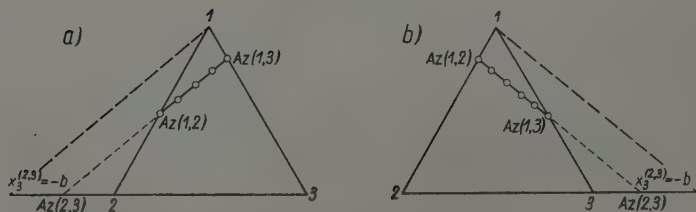


Fig. 5. Series of ternary azeotropes lying between azeotropes $Az(1, 2)$ and $Az(1, 3)$

$$(a) \quad -b < x_3^{(23)} < 0, \quad b > 0,$$

$$(b) \quad -b > x_3^{(23)} > 1, \quad b < -1.$$

Therefore, for the system (1,2,3), the conditions of azeotropes tangent at the corner of the triangle are:

$$(8a) \quad x_1=1, \quad x_2=0, \quad x_3=0, \quad x_3^{(23)}=-b, \quad x_1^{(12)}=1, \quad x_1^{(13)}=1,$$

$$(8b) \quad x_2=1, \quad x_1=0, \quad x_3=0, \quad x_1^{(13)}=-c, \quad x_2^{(23)}=1, \quad x_2^{(12)}=1,$$

$$(8c) \quad x_3=1, \quad x_1=0, \quad x_2=0, \quad x_1^{(12)}=-a, \quad x_3^{(23)}=1, \quad x_3^{(13)}=1.$$

It follows that such a tangent azeotrope may be formed if two binary azeotropes are tangent at the same corner. If the azeotrope $Az(23)$ is not tangent in the series (1,2,3), the appearance of the ternary azeotrope tangent at the corner 1 is possible only if the mole fraction $x_2^{(23)}=-b$.

Remark. Comparison with experimental data, served, in general, to confirm our predications. A poor degree of agreement in the case of azeotropes formed by pyridine and acetic acid with the series of normal paraffins [9] was due to the association of acetic acid in both the liquid and the vapour phase.

Summary

1. On the basis of the equations relating the compositions of binary and ternary azeotropes [1], [3], the schemes of formation of series of ternary azeotropes of the types (1_i, 2, 3), (1_i, 2, 3_k) and (1_i, 2_j, 3_k) are given. (1_i), (2_j) and (3_k) represent three homologous series.

2. Conditions are formulated for the formation of two kinds of tangent ternary azeotropes (i. e., if the concentration of one or two components in the azeotropes tends to zero).

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Diffusion Constant of Hydrogen in Iron Cathodes

by

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Various investigators have attempted to determine the diffusion constant of hydrogen in iron and steel, but their efforts were mainly limited to the upper temperature range. As regards the rate of diffusion at low temperatures, incompatible views have been expressed.

Ham [1] observed, between 200 and 350°C., a profound change in the slope of the diffusion isobar of hydrogen in relatively pure iron; an increase in carbon content shifted this discontinuity to a lower temperature. Ham and Rast [2] suggested that these anomalies may be due to an electronic rearrangement in iron atoms and to a change of the binding forces between the iron atoms and hydrogen ions or excited atoms.

Sykes, Burton and Gegg [3] gave the value for the diffusion constant of hydrogen in iron at 20°C. extrapolated from the temperature range 1100 = 400°C. ($D_{20} = 1.5 \times 10^{-5}$ sq. cm./sec.); in the same article however, they emphasized that very considerable anomalies in permeability were likely to be encountered in iron below 350°C.

In a recent work, Stross and Tompkins [4] observed, between 150 and 900°C., no anomalies in the evolution rate of hydrogen from over-saturated iron samples.

A number of authors have suggested the existence of two distinct processes of hydrogen evolution from iron: a rapid evolution in the first stage, and a much slower evolution during the second stage [5]. Other writers mention the supposed existence of two forms of hydrogen, defined respectively as more readily and less readily diffusible [6]. Yet Demarez, Hock and Meunier [7] found at 650°C. no evidence of the existence of two different states of hydrogen in mild steel.

Experimental

In our experiments two different methods of determination of the diffusion constant of hydrogen in iron cathodes were used:

- (i) measurement of the rate of evolution of hydrogen,
- (ii) observation of the time period necessary to obtain the maximal stationary elongation of a cathodically polarised iron coil.

Using method (i), a sample of iron wire, 0.45 mm. in diameter and 1500 mm. in length, bent in the shape of a coil, was cathodically polarised in 1 N H_2SO_4 solution containing arsenic trioxide. After 1 hour of polarisation, the sample was washed rapidly and immersed in water at 20°C. The rate of gas evolution was measured at normal atmospheric pressure using a microburette.

Using method (ii), a coil made from annealed iron wire, 0.45 mm. in diameter and 300 mm. in length, was cathodically polarised at 20°C, in 1 N H_2SO_4 solution containing arsenic trioxide. The elongation of the coil due to hydrogenation [8], [9], was measured with a cathetometer.

For these experiments an iron wire was used in which the following impurities were present:

0.10% C, 0.03% Mn, 0.03% Si, 0.012% P and 0.030% S.

Calculations

After Barrer [10], the differential form of Fick's law, applicable for the sorption and desorption of a gas in and from long metal wires, is:

$$(1) \quad \frac{\partial C}{\partial t} = D \left[\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial C}{\partial r} \right) \right],$$

where C — concentration,

D — diffusion constant,

r — distance from the axis of the wire,

t — time.

At initial conditions

$$C = 0 \quad \text{for} \quad 0 \leq r \leq r_0,$$

where r_0 is the radius of the wire. If the boundary conditions are

$$C = C' \quad \text{for} \quad r = r_0 \quad \text{and} \quad t > 0,$$

the mean concentration \bar{C} of the gas, which diffuses across the section of the wire is given by the following equation:

$$(2) \quad \bar{C} = C' \left(1 - \frac{4}{r_0^2} \sum_{n=1}^{\infty} \frac{1}{d_n^2} e^{-D d_n^2 t} \right).$$

C' — constant concentration in the superficial layer,

α_n — the successive roots of the equation,

$$J_0(\alpha_n r_0) = 0,$$

J_0 — zero order, first kind Bessel function.

The equation (2) is applicable for the saturation process of iron wires with cathodic hydrogen. Indirectly, it seems also to be applicable in discussion of the extent of elongation of iron wires due to hydrogenation.

Let us assume that

(i) the slowest phenomenon which determines the rate of elongation of the wire is the radial diffusion of hydrogen;

(ii) the stationary state of elongation, which does not depend upon the temperature, is reached for the wire of a given diameter at a constant relation of the mean concentration \bar{C} to the maximum superficial concentration C' :

$$(3) \quad \frac{\bar{C}}{C'} = \text{const.}$$

The equation (1) may also serve for the calculation of the rate of desorption of hydrogen from oversaturated iron wires. If the boundary conditions are

$$C' = 0 \quad \text{at} \quad r = r_0 \quad \text{for all} \quad t,$$

and the initial condition

$$C = f(r) \quad \text{at} \quad 0 \leq r \leq r_0 \quad \text{for} \quad t = 0,$$

then the velocity of desorption will be

$$(4) \quad \frac{dv}{dt} = -2\pi \frac{d}{dt} \int_0^{r_0} cr dr = \frac{4\pi}{r_0^2} \sum_{n=1}^{\infty} D \alpha_n^2 e^{-D \alpha_n^2 t} \int_0^{r_0} \frac{rf(r) J_0(\alpha_n r) dr}{[J_0'(\alpha_n r_0)]^2} - J_0(\alpha_n r) r dr.$$

For long time periods, especially for a thin wire, the sum in the equation (4) reduces to the first expression

$$(5) \quad \frac{dv}{dt} = -\frac{249.132D}{r_0^3} e^{-\frac{D}{r_0^2} 5.784t} \int_0^{r_0} \left[\int_0^{r_0} rf(r) J_0(2.405r) dr \right] J_0(2.405r) dr,$$

which leads to the approximative equation

$$(6) \quad \frac{d \log \frac{dv}{dt}}{dt} = -\frac{2.512}{r_0^2} D.$$

The equation (6) enables us to calculate the diffusion constant from measurements of the desorption rate of hydrogen from oversaturated iron wires. The initial condition assumed by the derivation of the equation (6) takes into account the possibility of an unequal state of saturation of the section of the wire by the hydrogen. This fact is of particular importance for our method of investigation, since, following interruption of the electrolysis prior to the beginning of measurements of the hydrogen desorption rate, there is a period during which the gas escapes rapidly from the wire. Equation (6) may be shown to be valid for time periods sufficiently long also when it is assumed, that boundary condition is $c = \text{const.} = 0$, at $r = r_0$ for all t' , in contrary to Geller and Tak-Ho Sun [6] assumption.

Results

Fig. 1 presents a typical curve of changes in the volume of evolved hydrogen as a function of time. Fig. 2 shows the results of the same experiment, but in this case the logarithm of the rate of desorption is

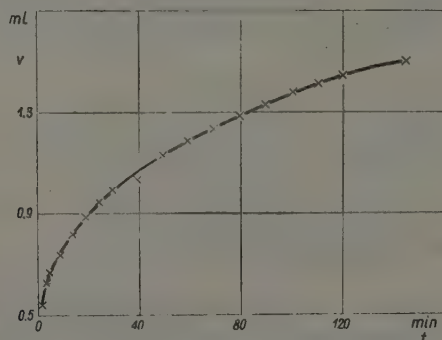


Fig. 1

plotted as a function of time. Two distinct stages of desorption are visible, with different diffusion constants.

The mean values of diffusion constants calculated from results of 10 experiments are as follows:

during the first stage of hydrogen evolution $D_I = 50 \times 10^{-8} \text{ cm.}^2 \text{ sec.}^{-1}$
 " " second " " " " $D_{II} = 9.6 \times 10^{-8} \text{ cm.}^2 \text{ sec.}^{-1}$

These values depend on the composition of the steel, and probably also on superficial conditions, that is on the kind of medium into which desorption occurs. The influence of these factors is to be the object of further investigations.

Our calculations, based on the time necessary to obtain the maximum stationary elongation of iron coils, lead to values of D lying in the

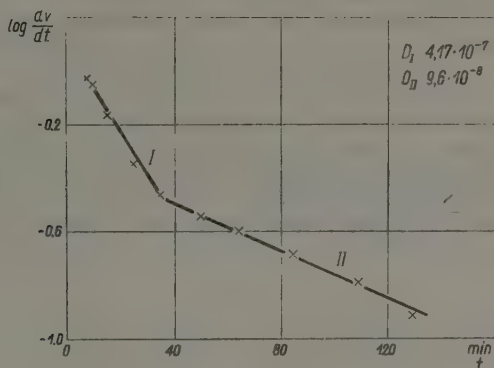


Fig. 2

same range of 10^{-7} to 10^{-8} cm.²/sec.⁻¹, if we assume that the stationary state of elongation of the wire is reached before the stationary state of saturation with hydrogen:

$$0.6 < \frac{\bar{C}}{C'} < 1.$$

To date, sufficient information is not available for a precise calculation of that value, since we do not know the saturation grade which corresponds to the maximum extent by stationary deformation of the iron cathode.

Conclusions

(i) The diffusion constant of hydrogen in iron at 20°C., calculated from results of measurements of the rate of desorption of hydrogen from cathodically oversaturated iron wire, is about 1/100 of the value extrapolated from results obtained by different investigators at high temperatures.

(ii) Two stages of desorption of hydrogen from iron wire immersed in water at 20°C. can be grasped. For the first stage $D_I = 5.0 \times 10^{-7}$, for the second stage $D_{II} = 9.6 \times 10^{-8}$ cm.²/sec.⁻¹.

(iii) The results confirm the view expressed in preceding papers [8], [9], to the effect that the extent of deformation in iron cathodes is determined by the process of penetration of hydrogen into the metal. The maximum stationary elongation of the wire is probably reached before the stationary state of saturation with hydrogen.

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The Electric Conductivity of NiO Catalyst in the Course of Ethyl Alcohol Dehydrogenation

by

A. BIELAŃSKI, J. DEREŃ, J. HABER, T. WILKOWA

Presented by B. KAMIENSKI on November 15, 1956

In previous communications [1]–[4] the authors reported on the results of their investigations on changes in the electric conductivity of some semiconducting oxide catalysts in the course of catalytic ethyl alcohol dehydrogenation. The catalysts used were pure *n*- or *p*-semiconductors as well as their mixtures. The behaviour of *n*-conducting oxides — ZnO, Fe₂O₃ and their mixtures — was qualitatively the same in all the region of temperatures used, i. e., the conductivity of the catalyst increased when reacting vapours were introduced.

As *p*-semiconducting oxide — besides MgO, which showed low conductivity — we used mainly Cr₂O₃. The behaviour of this oxide, however, appeared to be complicated. Up to about 450°C. its conductivity decreased, as one would expect. Above this temperature, conductivity first decreased and then increased up to a value higher than the initial one. According to the authors, this change in behaviour may be explained by a change from *p*- to *n*-type of conductivity. Such a change was in fact observed by Weisz, Prater and Rittenhouse in the course of cyclohexane dehydrogenation on chromia-alumina catalyst [5]. This effect seems not to be typical for *p*-semiconducting oxides; we therefore considered that an investigation of other *p*-semiconducting oxides was necessary. Nickel oxide was chosen for the present investigation. A brief survey of recent papers on its electronic properties has been given by Parravano and Boudart [6].

The present experiments were carried out in the same way as previously [1]. Nickel oxide was obtained by prolonged calcination of NiCO₃ (p. a. Merck) at 600°. The oxide was several times heated, cooled and ground in a mortar; then it was pressed into cylindrical pellets (diameter 12 mm., height 6 mm.) under a pressure of about 50 atm.

In order to compare the electric behaviour of our NiO with that of the NiO used by other authors we carried out a series of measurements of its conductivity in air within the temperature range of 100-650°.

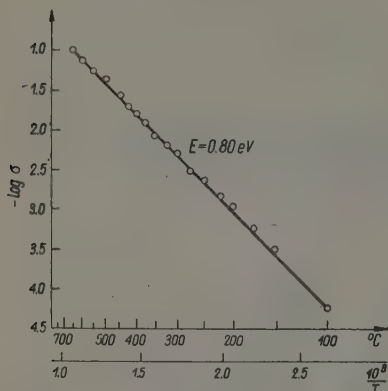
The $\log \sigma - 1/T$ diagram was linear as shown in Fig. 1, and the energy of activation calculated from the equation

$$\sigma = A \exp(-E/2kT)$$

for various samples was from 0.73 to 0.81 eV. These values, as well as the shape of the $\log \sigma - 1/T$ diagram, are in good agreement with the results given by Hoggarth [7].

After vapours of the 20% (vol.) alcohol-water mixture had been introduced into the reaction chamber, the electric conductivity of the catalyst decreased and after 10-15 minutes reached a new constant value. The course of such an experiment, carried out at 275°, is shown in Fig. 2.

Fig. 1. Logarithm of conductivity of NiO in air as a function of the reciprocal of absolute temperature



As previously, also in the present investigation, we found besides water and alcohol, only acetaldehyde in the condensation products. When

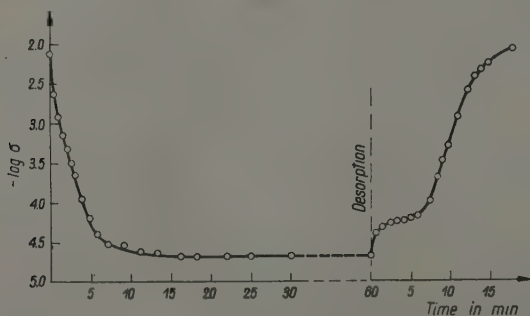


Fig. 2. Change in $\log \sigma$ of the NiO catalyst in the course of the reaction of dehydrogenation of ethyl alcohol vapours. Reaction temperature 275°C

the current of flowing vapours was cut off, and air was again introduced at the initial pressure of 10 mm. Hg the conductivity also rose back to its initial value.

The decrease in conductivity of the NiO may evidently be explained by assuming that the chemisorbed molecules of the reagents behave as

donor centres at the surface of the catalyst. The electrons given by the donors recombine with the positive holes present in the boundary layer of the solid, thus diminishing the number of electric current carriers and causing a drop in the electric conductivity. This donating character of the chemisorbed molecules was also observed in our previous experiments on ethyl alcohol dehydrogenation on other semiconducting oxide catalysts.

Fig. 3 shows the $|\Delta \log \sigma|$ value (full line) and the catalytic reaction yield k (dotted line) as a function of temperature. As measure of the catalytic reaction yield we took the number of milligrams of CH_3CHO formed when 20 ml. of 20% alcohol-water mixture was passed through the reaction chamber.

The $|\Delta \log \sigma| - k$ plot is shown in Fig. 4. The dependence of both values is linear up to 300° , similarly as it was in our previous experi-

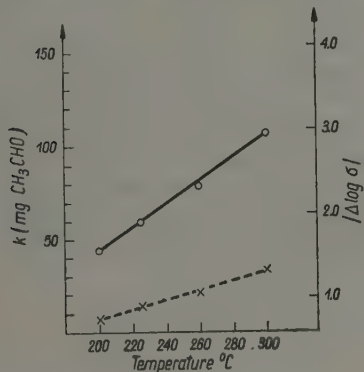


Fig. 3. Changes in the $|\Delta \log \sigma|$ value (full line) and the catalytic reaction yield (dotted line), both as a function of the reaction temperature

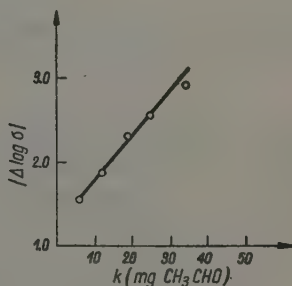


Fig. 4. The $|\Delta \log \sigma|$ values as a function of the reaction yield k

ments with other semiconducting oxides, and may be expressed by the equation

$$|\Delta \log \sigma| = A + B \cdot k.$$

Above 300° , the electric conductivity of the NiO catalyst first decreased, similarly as it did at lower temperatures, but after a few minutes (this period of time was the shorter, the higher was the temperature) the decrease was followed by a sudden increase up to a value higher than the initial one. This process is illustrated by the diagram in Fig. 5, showing the results obtained at 350° . The initial decrease in conductivity of the working catalyst, followed by its increase, was also observed in the case when pure Cr_2O_3 or Cr_2O_3 -rich oxide mixtures were used above 500° [2]. There is, however, an essential difference between

the two cases. After desorption, the conductivity of Cr_2O_3 or Cr_2O_3 -rich catalysts assumed the initial value and when water-alcohol vapours were again let in, the same process was repeated, i. e., we observed the decrease in conductivity followed by its increase. On the contrary, the conductivity of NiO did not resume its initial value even after prolonged desorption. This shows that the mechanisms of both processes were different.

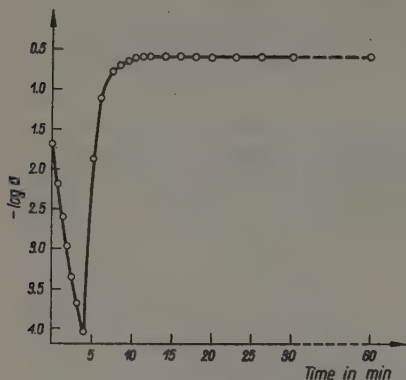


Fig. 5. Change in $\log \sigma$ of the NiO catalyst in the course of the reaction of ethyl alcohol dehydrogenation. Reaction temperature 350°

became ferromagnetic. The electric resistance of such a pellet was characterised by a positive temperature coefficient amounting to about 0.003, which was also the value observed for metallic nickel. The absolute value of the resistance of the pellet, which was about 10 ohms, showed however that the pressed grains of nickel oxide were covered with a very thin layer of the metal.

Some additional information about the properties of the reduced layer could be also obtained when a superficially reduced pellet was heated in air at normal pressure and its electrical conductivity was measured simultaneously. The results of these measurements are shown in Fig. 6. At each temperature, the sample was heated until the conductivity was constant. It lasted several minutes.

Portion *a* of the plot, showing the increase in conductivity from the value which was observed when the catalytic reaction was inter-

As already mentioned, the behaviour of Cr_2O_3 may be explained by inversion of the conductivity from *p*-to *n*-type. In the case of NiO we have to deal with a surface reduction of the oxide to metallic nickel. After the reduction took place the surface layer of the catalyst, about 2 mm. deep, changed its colour from grey-green to blue-black and be-

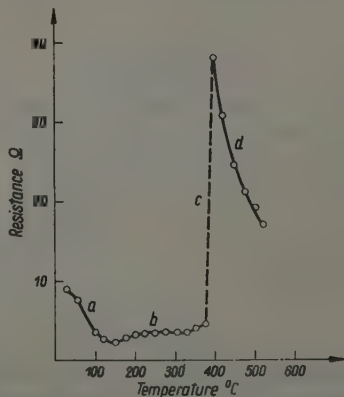


Fig. 6. Change in the resistance of superficially reduced NiO catalyst in the course of heating in air at normal pressure

rupted, up to the value of about 2 ohms, probably corresponds to the desorption of the rest of adsorbed reagents. The conductivity, decreasing with temperature, corresponding to portion *b* of the curve is, according to our view, controlled by the conductivity of the layer of metallic nickel covering the grains of NiO. As already mentioned, the temperature coefficient of the resistance is of the same order as in the case of metal.

Above 350°, the conductivity drop was observed down to the value noted in air before the pellet was used as the catalyst (portion *c* of the

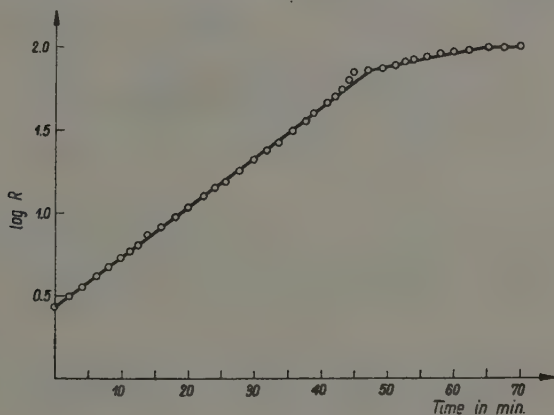


Fig. 7. Change in the logarithm of resistance in the course of oxidation at a temperature of 360°, as a function of time

curve). The last portion of the curve (*d*) shows a linear increase of the $\log \sigma$ -value with a decrease of $1/T$. The energy of activation of electric conductivity as calculated from this portion (0.66-0.75 eV) was practically the same as that found for NiO in air (Fig. 1). The surface layer of the sample after heating in air changed its colour back to grey-green. All these facts show that portion *c* corresponds to the oxidation of the surface layer of the pellet and portion *d*, to the measurements carried out with the sample, the conductivity of which was determined by the conductivity of NiO only.

The measurements of the conductivity were also carried out in the course of oxidation at a constant temperature. In our experiment, carried out at 360°, we found that the $\log \sigma$ -value changed linearly with time (Fig. 7).

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Further Remarks on the Structure of Aniline Black on the Basis of Infra-Red Absorption Spectra

by

T. URBĄŃSKI and K. SZYC-LEWAŃSKA

Presented by T. URBĄŃSKI on November 20, 1956

Continuing our experiments on the structure of emeraldine and aniline black previously reported [1], we have now examined the infrared absorption spectra of the compounds: emeraldine pernigraniline (aniline black), ungreenable aniline black, anilinoquinone, dianilinoquinone and phenazine.

All these compounds have been examined in the Hilger single beam spectrophotometer with optics of sodium chloride. All compounds

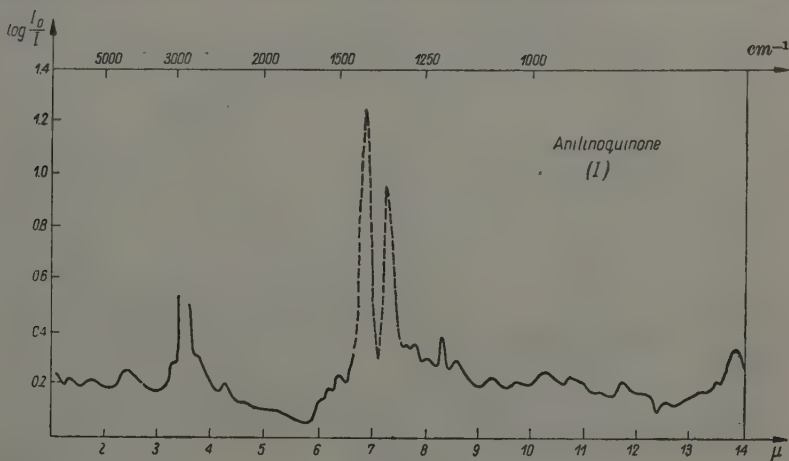


Fig. 1

were used in the form of mull in paraffin oil, the ratio of the substance to the oil being 1/20. The thickness of the layer was 0.02 mm.

The results are tabulated below and the absorption curves are reproduced in Fig. 1-6.

All absorption spectra of the compounds (I)–(V) show great similarity in the whole region examined.

The absorption spectrum of phenazine (VI) is similar to those of compounds (I)–(V) in the range from $1\ \mu$ to c. $10\ \mu$. From c. $10\ \mu$ to $14\ \mu$

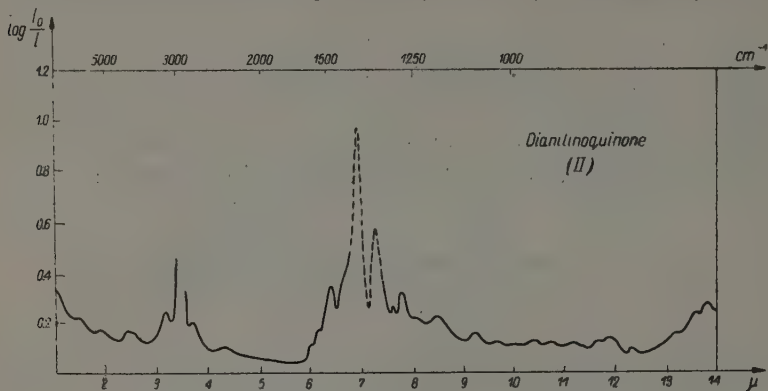


Fig. 2

the absorption curve of phenazine is distinctly different from those of anilinoquinones (I)–(II) and of the products of various stages of formation of aniline black (III–V.)

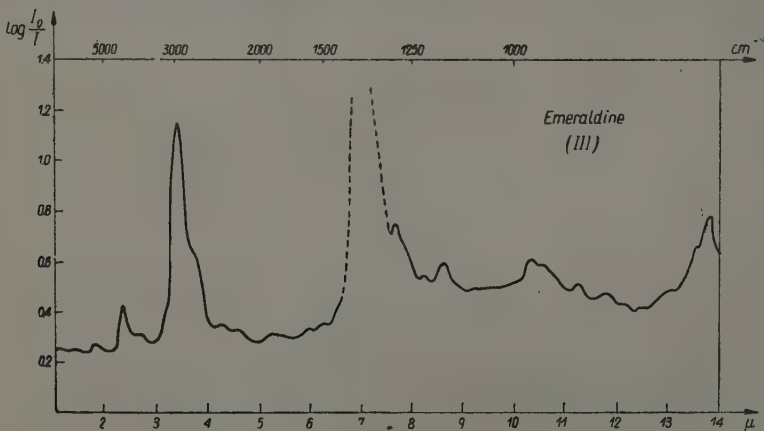


Fig. 3

The following interpretation of the absorption bands could possibly explain the similarity and differences in the structure of the compounds. (The wide and strong bands in the regions $1460\text{--}1480\text{ cm}^{-1}$ and $1330\text{--}1390\text{ cm}^{-1}$ should not be taken into consideration since they belong to the paraffin oil (vibrations of CH_2 and C-CH_3)).

(1) The wide and strong band between 2985 or 2940 and 2780 or 2740 or 2700 cm^{-1} should very likely be assigned to C—H aromatic stretching vibrations. It exists in the spectra of all six compounds.

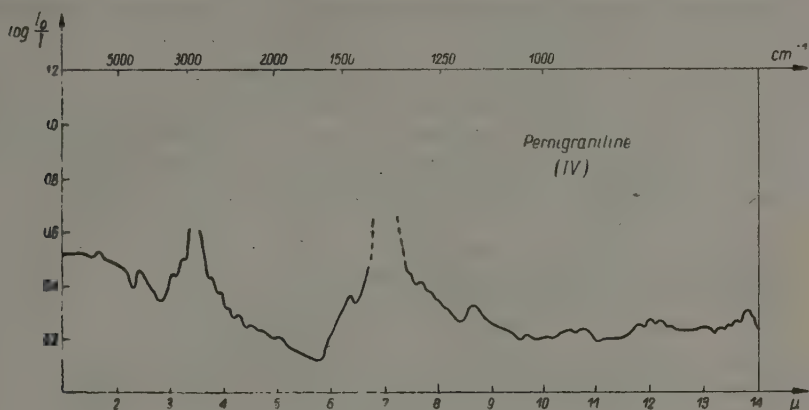


Fig. 4

(2) A weak band 1667 cm^{-1} which exists in the spectra of compounds (I)–(V) probably belongs to the vibrations of C=O groups in quinones. It does not exist in the spectrum of (VI).

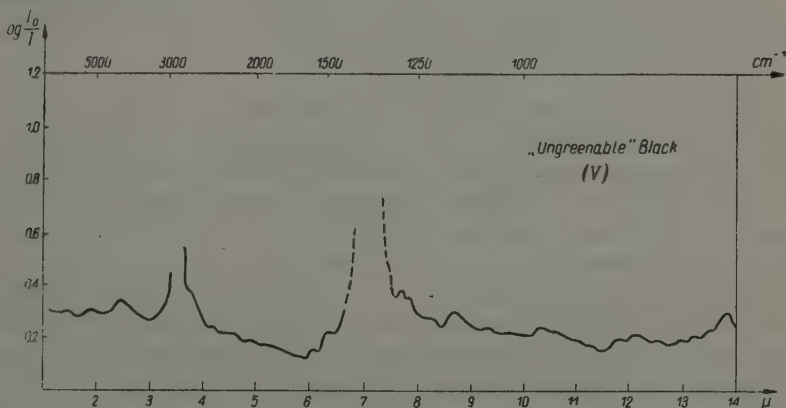


Fig. 5

The band with wave number 1613 cm^{-1} and the "shoulder" with wave number 1515 cm^{-1} , which exist in the spectra of the compounds (I)–(III) should probably be ascribed to $>\text{NH}$ deformation vibrations. They cannot be detected in the absorption curves of (IV) and (V).

This may indicate that the secondary aminogroups, which exist in

anilinoquinones (I) and (II) and probably in emeraldine would disappear in the course of the oxidation of emeraldine to pernigraniline, and they are still absent in the "ungreenable" black.

(4) The frequencies 1563, 1575, 1587 and 1600 cm^{-1} which exist in the spectra of all compounds: (I), (II)–(III), (IV)–(V) and (VI), respectively, are probably produced by the conjugated aromatic rings [2].

(5) Two bands, one in the region 1333–1290 cm^{-1} and another in the region 1299–1274 cm^{-1} are probably produced by the vibrations of the bond C–N between the aromatic ring carbon and nitrogen of the secondary or tertiary amino group. They exist in all six spectra.

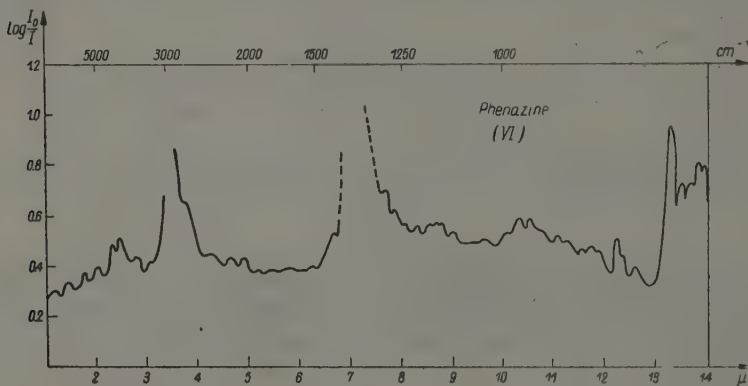


Fig. 6

(6) The relatively strong bands 1176 (compounds (I)–(III)), 1163 (IV) and 1156 cm^{-1} (V) cannot be assigned with certainty. It is not improbable that they are due to carbonyl stretching vibrations in quinones [3].

In any case they are distinctly different from the broad band (with three weak maxima) in the region 1176–1130 cm^{-1} , which exists in the phenazine absorption curve (VI).

(7) The absorption spectra of the compounds (I–V) show a number of bands with frequencies near to 1000 cm^{-1} . Similar bands are present in the spectrum of the compound (VI), but they slightly differ in both number and frequencies.

Thus the compounds (I)–(V) show three bands in the regions: 1087–1081 cm^{-1} , 1041–1020 cm^{-1} , 971–966 cm^{-1} . Five bands in the same region of the spectrum of the compound (VI) are: 1111, 1075, 1036, 990, 966 cm^{-1} .

They are probably produced by the vibrations of aromatic ring. It is well known that their frequencies depend on the position of substituents [2]. The frequencies of these bands suggest substitution in the positions:

1.2, 1.4, 1.2.4., 1.3 and also monosubstitution.

TABLE

No. of diagram	Substance	Absorption frequencies cm^{-1} (s) — strong, (m) — medium, (sh) — shoulder
1	Anilinoquinone (I)	6667, 4167 (m), 2985-2778 (s), 2703 (sh), 2326 (m), 2151, 2000, 1667, 1613, 1563 (m), 1515 (sh), 1460 (s), 1379 (s), 1316, 1290, 1227, 1176 (m), 1081 (m), 1020, 971 (m), 930, 889, 862 (m), 813, 800, 758, 743, 722 (m)
2	Dianilinoquinone (II)	5714, 4167 (m), 2985-2778 (s), 2703, 2326, 2105, 2000, 1667, 1613, 1575 (m), 1515 (sh), 1460 (s), 1379 (s), 1316, 1290, 1205, 1176 (m), 1081 (m), 1026, 966, 930, 889, 862 (m), 840 (m), 816, 758, 738, 720 (m)
3	Emeraldine (III)	5714, 4167 (m), 2985-2778 (s), 2665 (sh), 2353, 2174, 1980, 1667, 1613, 1575, 1515 (sh), 1481-1379 (s), 1316, 1282 (sh), 1212, 1176 (m), 1081, 1031, 966 (m), 930, 881 (m), 851, 826, 813, 758, 736, 720 (s)
4	Pernigraniline (IV)	6061, 4082 (m), 2985-2740 (s), 2632, 2353, 2174, 2000, 1667, 1587, 1460-1389 (s), 1333, 1299, 1220, 1163 (m), 1087, 1042, 971, 930, 893, 848, 836, 823, 816, 813, 766, 752, 736, 722 (m)
5	"Ungreenable" Black (V)	5556, 4167 (m), 2985-2740 (s), 2632 (sh), 2353, 2128, 2000, 1667, 1587, 1471-1389 (s), 1307, 1274, 1212, 1156 (m), 1081, 1031, 971, 930, 889, 855, 826, 810, 775, 764, 758, 741, 720 (m)
6	Phenazine (VI)	6667, 5556, 4878, 4348, 4167 (m), 2941-2740 (s), 2667 (sh), 2353, 2273, 2174, 2041, 1905, 1835, 1600, 1481-1333 (s), 1290, 1274, 1205, 1176-1130, 1111, 1075, 1036, 990, 966 (m), 952, 939, 901, 889, 865, 851, 8440, 826, 816, 806, 796, 752 (s), 738, 727, 722 (m), 717 (m)

However, the bands do not seem to be very characteristic and cannot be taken as a proof of the anilinoquinone structure of (III), (IV) and (V). But there is great similarity between these bands in anilinoquinones (I)–(II) and in emeraldine and aniline black (II)–(V). On the contrary, the bands of phenazine (VI) differ considerably from those of (III)–(V).

(8) The bands with frequencies 862–851 cm^{-1} , 816–810 cm^{-1} and intermediate frequency (e. g., 840, 826 cm^{-1}) are most likely due to the aromatic C–H out of plane vibrations [3], [4]. They could not be assigned to *para* substitution, as they are also present in phenazine (VI).

(9) Two bands present in all the compounds examined, 758–752 cm^{-1} and 743–736 cm^{-1} , seem to be of importance, as they would confirm that the main position of the substituents is 1.2 (in the case of all the compounds examined) and 1.2.4 (in the compound (I)–(V)).

(10) The band 722–717 cm^{-1} in all compounds would suggest mono substitution. This is clear in the case of the anilinoquinones (I)–(II), where the $-\text{NH C}_6\text{H}_5$ group should give such a band.

Conclusion

The similarity of the infra-red absorption spectra of emeraldine, pernigraniline and "ungreenable" aniline black with the absorption spectra of anilinoquinone and dianilinoquinone seems to confirm the suggestion expressed formerly, that emeraldine, pernigraniline and "ungreenable" aniline black may possess the structure of dianilinoquinone.

Moreover, the quinoneimine structure of emeraldine and pernigraniline could not be confirmed, because of the lack of band characterising the aminogroup ($3200\text{--}3400\text{ cm.}^{-1}$) in their absorption spectra.

The phenazine structure of "ungreenable" aniline black could not be confirmed by comparison with the absorption spectrum of phenazine.

Further experiments will be carried out.

The authors are much indebted to Mrs. J. Świętosławska, Miss T. Krackiewicz and Miss B. Kontnik for carrying out the experiments on infra-red absorption spectra.

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On Ultraviolet Absorption Spectra of Some Nitro- and Halogenonitrodiols

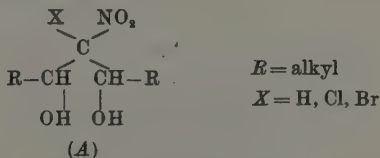
by

T. URBĄŃSKI, W. SOBÓTKA and Z. ECKSTEIN

Presented by T. URBĄŃSKI on December 1, 1956

In one of our former papers we pointed out to the influence of atoms of chlorine and bromine upon the ultraviolet absorption spectra. The increase of the van der Waals radius of halogen produced a decrease in the intensity of the band characteristic for the nitrogroup [1]. Also in another experiment the ionic iodine atom produced a marked reduction in the intensity of the NO_2 band [2], [3].

In order to continue this line of research, a series of nitro- and halogenonitrodiols-1,3 of the general formula (A) were examined, with a view to observe the influence of the length of the alkyl (R) or of the halogen (X) on absorption spectra.



The compounds (A) were now prepared by the method already described in the literature, which consists in aldolic addition of aldehydes to nitro- or halogenonitrocompounds in presence of the basic catalyst.

The products thus obtained are tabulated below (Table I). Products (V) and (VI) are new to the literature.

Fig. 1 shows ultraviolet absorption curves of 5-nitro-4,6-nonanediol (V) and 5-nitro-2,8-dimethyl-4,6-nonanediol (VII). They possess weak NO_2 maxima ($\Delta\epsilon=2$) between 270 and 280 $\text{m}\mu$. The bands are weaker than those of corresponding nitroparaffins, which show a difference of extinction $\Delta\epsilon=9.6-9.4$.

The weakening of the maxima is in agreement with the fact previously observed in diols and ascribed to the formation of two hydrogen

bonds between the nitrogroup and both hydroxyl groups [2], [3]. In the case of compounds (V) and (VII) the hydrogen bonds are probably wea-

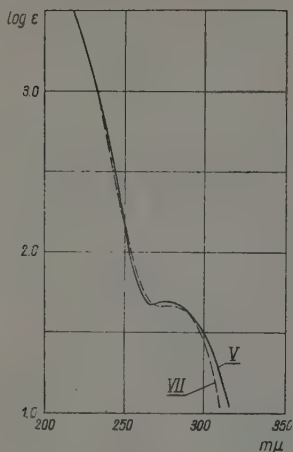


Fig. 1

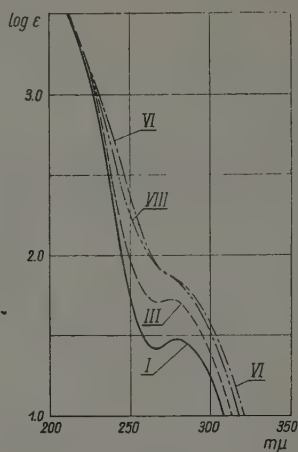
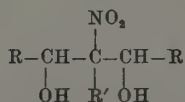


Fig. 2

kened, judging from the fact that slight NO_2 maxima are still present in the spectrum-curve of these compounds. This is probably produced by R more bulky than H .

Fig. 2. shows absorption curves of chloronitrodiols (compounds (I), (III), (VI) and (VIII)). They all possess 265–280 $m\mu$ bands, characteristic

TABLE I



Compound	R	R'	m. p. °C.	References
I	H—	Cl—	117	[3]
II	H—	Br—	120	[4]
III	CH_3 —	Cl—	118	[5]
IV	CH_3 —	Br—	110	[5]
V	$n\text{-C}_2\text{H}_5$ —	H—	70	—
VI	$n\text{-C}_2\text{H}_5$ —	Cl—	96	—
VII	$(\text{CH}_3)_2\text{CH}-\text{CH}_2$ —	H—	93	[6]
VIII	$(\text{CH}_3)_2\text{CH}-\text{CH}_2$ —	Cl—	126	[6]
IX	$(\text{CH}_3)_2\text{CH}-\text{CH}_2$ —	Br—	134	[6]

for the nitrogroup. The deepest maximum ($\Delta\epsilon=4$) is given by 2-nitro-2-chloro-1,3-propanediol (I). An increase of the alkyl R reduces the depth of the maximum, which in some chloronitrodiols (VI) and (VIII) is changed into a bend.

The introduction of bromine into the diol molecule produces a considerable weakening of the NO_2 bands and thus the maxima of the absorption curves of the compounds (II), (IV) and (IX) are transformed into the bends at $275\text{--}280\text{ m}\mu$ (Fig. 3). This would confirm the former observation that an increase in halogen van der Waals radius considerably reduces the intensity of the maximum of absorption characteristic for the nitrogroup.

The main characteristics of the absorption curves are tabulated in Table II. All compounds were examined in ethanolic solutions.

The authors are much indebted to Mrs. J. Świątosławska, Miss D. Ciecierska and Miss K. Gorczyńska of the Institute of General Chemistry, Warsaw, for carrying out experiments on ultraviolet absorption spectra in a Beckman spectrophotometer.

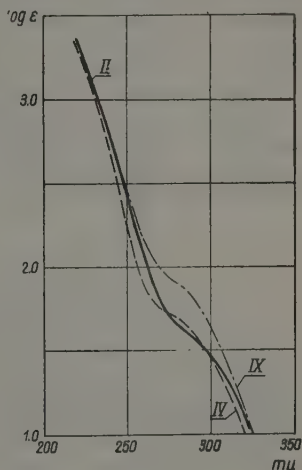


Fig. 3

TABLE II
Characteristics of the absorption spectra

Compound	λ min.	ϵ min.	λ max.	ϵ max.	$\Delta\epsilon$
I	265	27	280.2	31	4
II			280 *)	46.6	
III	265	52	275	54	2
IV			275 *)	54	
V	268	49	276	51	2
VI			275 *)	76	
VII	270	48	280	50	2
VIII			275 *)	75	
IX			278 *)	84.5	

Experimental

5-Nitro-4,6-nonanediol (V)

1-Nitro-2-pentanol (33.3 g., 0.25 mol.) was mixed with butyraldehyde (27 g., 0.37 mol.); a small amount of triethylamine, to obtain pH c. 7, was added, and all was left for a fortnight at room temperature. The solution was then neutralised with

*) a bend.

diluted hydrochloric acid and extracted with ether. The ethereal solution was washed with potassium hydrogen carbonate aqueous solution and dried over sodium sulphate. Ether and unreacted nitropentanol were removed by distillation (the latter under pressure of 1 mm. Hg, at 135° bath temperature). The residue solidified into 12.2 g. of crude product (V), which was crystallised from carbon tetrachloride, m. p. 70°. (Found: C 49.7, H 8.7, N 6.9%; $C_8H_{15}O_4N$ required: C 49.3, H 8.6, N 6.8%).

The compound readily formed cyclic acetal, when warmed with benzaldehyde in benzene solution in presence of a small quantity of benzenesulphonic acid, following the method formerly described [6]. 5-nitro-4,6-di-*n*-propyl-2-phenyl-1,3-dioxane thus formed, is a white crystalline compound, m. p. 75.5-76.5°; it exhibited the pseudo-nitrol reaction. (Found: N 5.3%; $C_{16}H_{23}O_4N$ required: N 5.05%).

5-Nitro-5-chloro-4,6-nonanediol (VI)

1-Nitro-1-chloro-2-pentanol (8 g., 0.05 mol.) and butyraldehyde (7 g., 0.1 mol.) were mixed, and triethylamine (1.5 ml.) was added, to obtain *pH* c. 7. The solution was left at room temperature for 4 days. It was then neutralised with diluted hydrochloric acid and extracted with ether. The ethereal solution was washed with aqueous potassium hydrogen carbonate and dried over sodium sulphate. Ether and unreacted nitrochloropentanol were removed by distillation (the latter at 95° under 1 mm. Hg). The residue formed 5.7 g. of the crude product (VI), which was crystallised from carbon tetrachloride, m. p. 96° (Found: N 5.8%; $C_8H_{18}O_4NCl$ required: N 5.9%).

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On the Properties and Preparation of 1-Cycloheptenylnitromethane

by

Z. ECKSTEIN, A. SACHA and T. URBANŃSKI

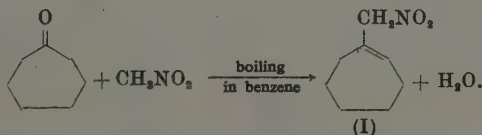
Presented by T. URBANŃSKI on December 1, 1956

It is well known that the reaction of some cyclic ketons with nitroparaffins in the presence of strongly basic catalysts leads to the formation of nitroölefins under elimination of a mol. of water. The yield of nitroölefin depends on the base used as a catalyst and on specific properties of cyclic keton. When cyclopentanone is used [1], the yield of nitroölefin is low and the product is not very stable, being readily subjected to polymerisation. Much better results were obtained in the case of cyclohexanone [1]–[4] and its methyl derivatives [5], [6]. Sufficiently stable nitromethylcyclohexene derivatives have been formed with good yield.

It seemed of interest from both theoretical and practical aspect to investigate the reaction of a larger ring ketones with nitroparaffins.

The first series of experiments included the reaction of cycloheptanone (suberon) with nitromethane in presence of piperidine as a catalyst. It has now been found that this first member of the larger ring ketones reacted much more slowly with nitromethane, when the reaction conditions were the same as in the case of cyclohexanone [5], [8]. Thus, 7.2 per cent nitroölefin (I) was formed after 12 days at room temperature, and 14 per cent yield was obtained after 18 days at 45–50°.

We succeeded in increasing the yield of (I) up to c. 60 per cent by dissolving the reaction mixture in benzene, heating the solution to boiling temperature and distilling the water formed in the course of the reaction:



This reaction is not reversible and the elimination of water was used to indicate the trend of the reaction.

1-Cycloheptenyl nitromethane (I) is liquid, b.p. 84-85° (1.4-1.6 mm.Hg), $n_D^{20}=1.4896$. It is colourless, but changes into yellowish on prolonged standing. It has very little inclination to polymerise and this property helps to regenerate cycloheptanone and nitromethane which have not entered into the reaction.

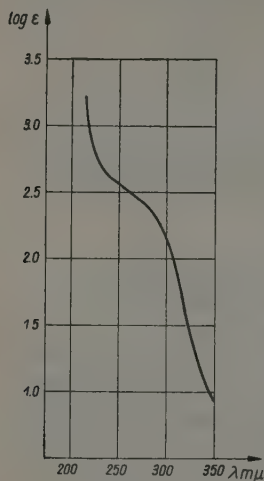


Fig. 1

The ultraviolet absorption spectrum of (I) was examined (Fig. 1) by Miss D. Ciecierska and Miss K. Gorczyńska of the Institute of General Chemistry, Warsaw. It does not show the maximum typical for the aliphatic nitrogroup, but only a bend in the region of 240-300 mμ. To have a deeper insight into the structure of this nitroölefine, the infra-red absorption spectrum was determined by Miss T. Krackiewicz and Miss B. Kontnik (Institute of General Chemistry). A Hilger spectrophotometer was used with NaCl optics, the thickness of the layer of the liquid being 0.08 mm.

The results (wave numbers of the bands) are tabulated (Table I) and shown in Fig. 2.

Both bands characteristic for the nitro group (1562 and 1379 cm.⁻¹) are present and so is the 1666 cm.⁻¹ band characteristic for the C=C

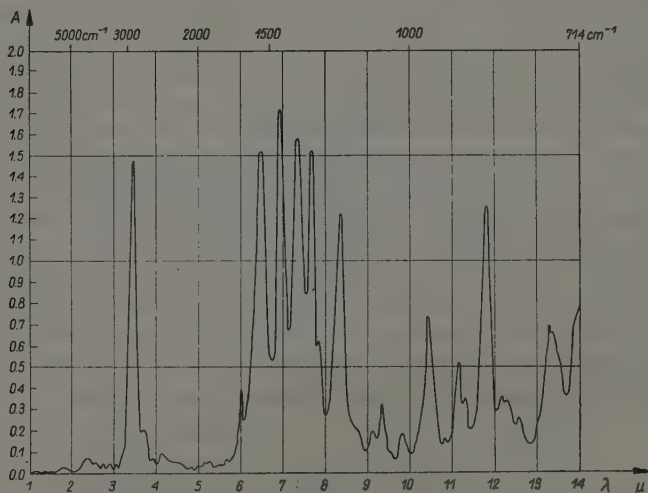


Fig. 2

bond in cycloaliphatic hydrocarbons; all are in agreement with the structure (I).

It is difficult, for the time being, to establish the reason why no maximum of the NO_2 group exists in the ultraviolet absorption curve. It seems that such an anomaly could be ascribed to the system

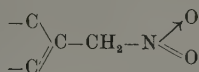


TABLE I

Characteristic frequencies and absorptions of the infra-red maxima of 1-cycloheptenylnitromethane

Wave number (in cm^{-1})	$\log \frac{I^0}{I}$	Assignment
8620	0.0094	
7692	0.0080	
5555	0.0270	
4255	0.0749	
2898	1.4438	C—H stretching
2702	0.2076	
2439	0.0941	
1666	0.3606	C=C in cycloaliphatic compounds
1562	1.5087	NO_2 asym. stretching
1449	1.7212	$\text{---CH}_2\text{---}$ deform. of cycloaliphatic compounds
1379	1.5687	NO_2 symm. stretching
1306	1.5228	
1303	1.3872	
1196	1.2219	
1098	0.1939	
1072	0.3243	
1020	0.1869	
961	0.7212	
925	0.1599	
898	0.5228	
886	0.3467	
847	1.2440	
823	0.3566	
816	0.3467	
796	0.2637	
751	0.6861	
747	0.6537	

We have already noticed a similar effect when the ultraviolet absorption of 1-cyclohexenylnitromethane was examined [14], [15]. It ap-

pears that the separation of the nitro group from the C=C bond by means of a methylene group may lead to an effect similar to the one, which was produced by two hydroxylic groups [9]–[13] or by the introduction of bromine into the α -position in nitroalcohols [16].

1-cycloheptenylnitromethane reacts readily with aliphatic or aromatic aldehydes in a manner typical for primary nitroparaffins.

In addition to 1-cycloheptenylnitromethane, a crystalline by-product was also obtained during the reaction described above. It will be subjected to examination.

Preliminary experiments with higher homologues of nitromethane and cycloheptanone also brought about a reaction with the elimination of water and basic products, but no nitroolefins were formed.

The results of the experiments mentioned above will be reported in due course.

The authors are much indebted to Mrs. J. Świątosławska, head of the Physical Department, Institute of General Chemistry, Warsaw as well as to Miss D. Ciecierska, Miss K. Gorczyńska, Miss B. Kontnik and Miss T. Kraczkiewicz for carrying out the experiments on absorption spectra.

Experimental

1-cycloheptenylnitromethane (I)

Method A. Suberon, obtained by the known method [7], and nitromethane were mixed in the molar ratio 1:2 in the presence of piperidine by the method described for cyclohexanone, using anhydrous magnesium sulphate to bind water formed during the reaction [5]. After 6 days of standing at room temperature no nitroolefine was detected in the products of the reaction. The reaction mixture was left for 12 more days and the product (I) was isolated by distillation. Another sample was, in addition, warmed occasionally to c. 50° for 18 more days. The yields are given in Table II.

Method B. Cycloheptanone (suberon) (50 g. — 0.32 mol.) was mixed with nitromethane (56 g. — 0.91 mol.). Anhydrous benzene (100 ml.) and piperidine (4 ml.) were then added and the resulting solution was heated on a steam bath. A still-head for collecting water was used. After c. 7.5 ml. water were collected in the still-head, the mixture was distilled under reduced pressure. Benzene and unreacted nitromethane was distilled at 30–35° under 10–15 mm. Hg. Product (I) was collected at 81–81.5° under 1–1.2 mm. Hg. The crude product was redistilled and the pure fraction was collected at 84–85° under 1.4–1.6 mm. Hg.

It is a colourless liquid, with a faint but characteristic turpentine-like smell. It decolorises bromine solution in carbon tetrachloride, dissolves readily in aqueous sodium hydroxide solution in a way typical for nitroparaffins.

Analysis: $n_D^{20} = 1.4896$ $d^{20} = 1.0600$ $R_{MD}(C_8H_{13}O_2N)$ — found 42.1
calculated 42.2 $C_8H_{13}O_2N$ required N 9.0 per cent
found N 8.9 „ „

TABLE II

Yield of 1-cycloheptylnitromethane in various condition of the reaction

Nr. method	Quantity of reagent				Reaction time	Yield		n_D
	CH_3NO_2 g.	suberone g.	piperi- dine ml.	benzene ml.		g.	%	
1/A.	28	25	2	—	12 days	2.5	7.2	1.4865
2/A.	28	25	2	—	18 days	5.8	14.2	1.4900
3/B.	28	25	2	50	48 hours	7.8	22.5	1.4890
4/B.	28	25	2.5	50	40 hours	19.1	55.1	1.4872
5/B.	28	25	2.5	50	30 hours	15.0	43.3	1.4896
6/B.	60	50	5	100	40 hours	37.0	53.3	1.4892
7/B.	56	50	4	100	24 hours	40.0	57.7	1.4895
8/B.	56	50	4	100	23 hours	42.0	60.6	1.4875
9/B.	120	100	10	240	24 hours	89.0	64.0	1.4899
10/B.	120	100	10	240	25 hours	80.0	57.6	1.4890

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On Endo- and Exoisomers of Nitroölefins (1-Cyclohexenyl- and Cyclohexylidenenitromethane). I

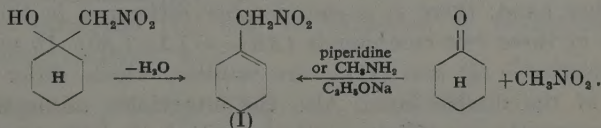
by

Z. ECKSTEIN, T. URBAŃSKI and H. WOJNOWSKA

Presented by T. URBAŃSKI on December 10, 1956

In order to find a more convenient method of preparing 1-cyclohexenylnitromethane (I) we examined the methods described so far in the literature. All of them are rather troublesome and the yields are low. They consist in dehydration of 1-nitromethyl-1-hydroxycyclohexane (further called "nitroalcohol"). When phosphorous oxychloride is used [1], the yield of (I) is c. 55 per cent. A better yield (70-75 per cent) can be obtained using thionyl chloride [1], [2]. The drawback of this method lies in the difficulty of obtaining the pure substance, as the repeated distillation does not produce a desirable degree of purification. The physical constants of the product (I) according to the literature and according to our own experiments are tabulated below (Table I).

Pure nitroölefin (I) can be obtained directly from cyclohexanone and nitromethane using a strongly basic catalyst [1], [3], [5] or stoichiometric quantity of sodium ethoxide [6]:



The advantage of the piperidine method consists in its simplicity and the purity of the product, but the yield of (I) is not high.

We have now found that the best yield and high purity of (I) could be obtained by heating nitroalcohol with piperidine. This has not yet been described in the literature.

We also tried to obtain nitroölefin (I) by splitting off the molecule of acetic acid from the acetate of the nitroalcohol. This is a known method of preparing nitroölefins [7]. It consists in heating acetate of nitroalcohol, containing an atom of active hydrogen, attached to the carbon with the nitrogroup.

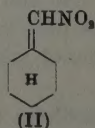
The method applied to the acetate of the nitroalcohol led to the formation of a new nitroölefin (II), different from 1-cyclohexenylnitromethane (I). The properties of two nitroölefins (I) and (II) are tabulated below.

TABLE 1
Comparison of properties of nitroölefins

Methods	Physical constants				References
	n_D^{20}	d^{20}	R_{MD}		
			found	calculated	
Dehydration of nitroalcohol by means of POCl_3	1.4856	1.0733	37.74	37.49	[1]
Dehydration of nitroalcohol by means of SOCl_2	1.4875	1.0788	37.66	37.66	—
Dehydration of nitroalcohol by means of piperidine	1.4860	1.0773	37.61	37.59	—
Condensation of cyclohexanone with nitromethane in presence of piperidine	1.4853	1.0699	37.82	37.49	[1]
	1.4838	—	—	—	[3]
	1.4865	1.0697	37.92	37.59	—
	1.48685	1.0761	37.71	37.59	*)
Olefinisation of acetate of 1-nitromethyl-1-hydroxycyclohexane	1.5073 ^{a)}	1.0853	38.72	37.59	—
	1.51375 ^{b)}	1.0867	39.09	37.59	*)
Isomerisation of nitroölefin (II) into (I) by means of diethylamine	1.4865	1.0690	—	—	—

^{a)} mixture (A); ^{b)} mixture (b).

The compound (II) has the same formula, calculated from the results of the elementary analysis, as the compound (I), i. e., $\text{C}_7\text{H}_{11}\text{O}_2\text{N}$. On the other hand, there is a considerable difference in the molecular refractions of these two compounds ($\Delta R_{MD} = 1.13\text{--}1.50$). It suggests that both nitroölefins — (I) and (II) — are isomers, which differ as regards the place of the double bond. Also the ultraviolet absorption spectra of both compounds are different. We suggested that the nitroölefin (II) has the structure of cyclohexylidenenitromethane:



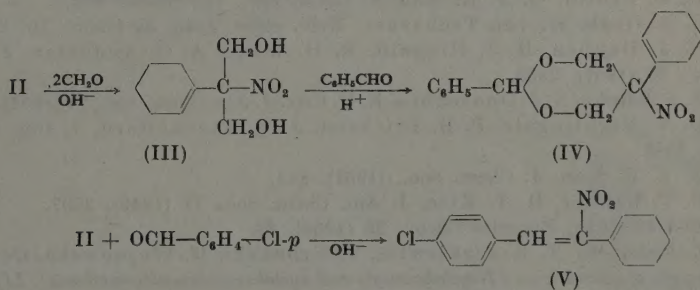
Both compounds differ from the point of view of some of their chemical properties. Thus, the compound (I) can readily be brominated,

*) determined by W. Sobótka.

forming 1,2-dibromo-1-nitromethylcyclohexane, and the compound (II) cannot be brominated in the same conditions.

On the contrary, both compounds (I) and (II) give identical products of base catalysed aldolic condensation with aldehydes. Thus, both compounds (I) and (II) reacted with formaldehyde in dioxane solution, in presence of triethylamine to form 2-nitro-2-(1-cyclohexenyl)-propane-1,3-diol (III), and this reacted with benzaldehyde to form 2-phenyl-5-nitro-5-(1-cyclohexenyl)-1,3-dioxane (IV). Both products — (III) and (IV) — were identical with those previously described [8].

The compound (II) reacted with *p*-chlorobenzaldehyde to form 2-nitro-2-(1-cyclohexenyl)-1-*p*-chlorophenylethene (V). The yield of (III) and (V) was as high as would be obtained from the pure nitroölefin (I).

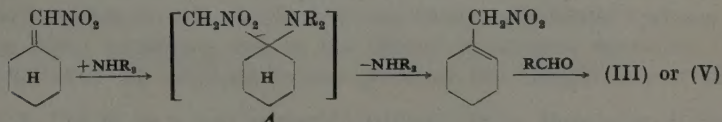


The product (V) did not lower the m. p. when mixed with the product previously obtained [8], by condensing 1-cyclohexenyl nitromethane (I) in the analogous conditions (in presence of *n*-amylamine, as catalyst).

The different conclusions could be drawn from the facts described above: either

(1) the nitroölefin (II) is a mixture, containing mainly 1-cyclohexyldenitromethane (II), or

(2) the nitroölefin (II) can be subjected to isomerisation under action of basic catalysts, e. g.:



We suggest here that an additive compound (A) would be formed from the *exo*-nitroölefin (II) and the base; then the compound (A) is cleaved into *endo*-nitroölefin (I) and the base. The compound (I) can react with aldehydes forming compounds of type (III) or (V).

We found that the substance (II), when subjected to the action of diethylamine or piperidine can be isomerised into (I) and this seems to give support to the hypothesis expressed by the diagram as above.

On the other hand, suggestion (1) is also true to some extent, since the infra-red absorption spectrum of the compound (II) [9] has shown that the compound (II), prepared from the acetic ester of the nitroalcohol, is a mixture of two nitroolefins, (I) and (II), in a ratio of about 1:10. This, however, would not account for the high yield of the products of reaction with aldehydes (III) and (V) and both hypothesis (1) and (2) should be accepted.

Experimental details will be reported elsewhere [10].

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